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TABLE OF CONTENTS

Vol. 27 May 1, 1944 No. 5

THE JOURNAL

Viscosity of Recent Container Glass 129–38

By H. A. Robinson and C. A. Peterson

Analysis of Cords and Stones 138–42

By G. J. Zarbo, H. J. Hunt, and D. C. Smith

Surface Tension and Persistence of Cords in Glass 143–45

By Mellen A. Knight

Surface Layer of Sheet Glass 145–48

By F. L. Bishop, Jr.

Rapid Method for Estimating Soda in Glasses, II 148

By S. R. Scholes and E. de R. Falcão

Fundamental Properties of Clay: VI, Flow Properties of Kaolinite-Water Suspension. 149–64

By F. H. Norton, A. L. Johnson, and W. G. Lawrence

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VISCOSITY OF RECENT CONTAINER GLASS*

By Howard A. Robinson and Charles A. Peterson

Abstract

A high-temperature, concentric cylinder viscometer has been constructed and calibrated. The calibration checks within 1% that obtained by Lillie for a similar apparatus and provides further evidence of the high degree of reliability of this type of measurement. The contention of Washburn and Shelton that the calibration in such instruments is a function of the viscosity is shown to be false. Because four independent investigations have been unable to check this contention, it may now be regarded as spurious. A medium temperature-range fiber viscometer for measuring the viscosity of glass in the annealing range has also been constructed. It is shown that the Fulcher equation, $\log \eta = -A + \frac{B}{T - T_0}$, fits the data obtained on the two instruments to within 0.5% for commercial soda-lime glasses. Complete viscosity data as a function of temperature are given for sixteen commercial container glasses, and the analyses are also included. These glasses show a wide range of viscosity.

I. Introduction

Experimental work in many laboratories during the past twenty years has shown that the viscosity of glass depends markedly on its chemical composition. Published data on glass viscosity, however, have not usually included accurate analyses, particularly when commercial glasses have been measured. Check tests among various laboratories have been sporadic and not infrequently carried out on glasses of "similar composition" rather than of identical composition. It would seem, therefore, to be of value to record in one place glass viscosities obtained over a period of the last three years and to describe the apparatus which has been built to measure them. Originally it was planned to include several additional glasses in this list, but, in view of the present press of defense work, it has been necessary to defer this project until after the war.

It is impossible to use a single piece of equipment to measure the viscosity of glass over the entire range of technical interest because apparatus which is capable of accurate measurement at 100 poise† can scarcely be suitable for measuring viscosity at 10^{16} poise. Three different pieces of apparatus actually have been used to cover this range. The first of these is a concentric cylinder apparatus similar to that described by Lillie.[1] This equipment may be used to measure viscosities between 100 and 3 million poise. A fiber viscometer similar to those described by Lillie,[2] Norton,[3] and Taylor[4] has been built for the region between 10^{10} and 10^{16} poise. In the region between 10^{6} and 10^{10} poise, the empirical softening-point furnace can be used to measure that temperature at which viscosity is equal to 4.5×10^{7} poise. These three pieces of equipment give viscosity values which lie on a single smooth curve.

* Presented at the Forty-Fifth Annual Meeting, The American Ceramic Society, Pittsburgh, Pa., April 21, 1943 (Glass Division). Received September 2, 1943.

† The singular form of "poise" is being used through this paper at the request of the author.

[1] (*a*) H. R. Lillie, "Measurement of Absolute Viscosity by Use of Concentric Cylinders," *Jour. Amer. Ceram. Soc.*, **12** [8] 505–15 (1929).

(*b*) H. R. Lillie, "Viscosity Measurements in Glass," *ibid.*, **12** [8] 516–29 (1929).

(*c*) H. R. Lillie, "Margules Method of Measuring Viscosities Modified to Give Absolute Values," *Phys. Rev.*, **36**, 347 (1930).

(*d*) H. R. Lillie, "High-Temperature Viscosities of Soda-Silica Glasses," *Jour. Amer. Ceram. Soc.*, **22** [11] 367–74 (1939).

[2] H. R. Lillie, "Viscosity of Glass Between Strain Point and Melting Temperature," *ibid.*, **14** [7] 502–11 (1931).

[3] F. H. Norton, "Measuring Viscosity of Glass," *Glass Ind.*, **16** [5] 143–44 (1935); *Ceram. Abs.*, **14** [7] 160 (1935).

[4] (*a*) N. W. Taylor and P. S. Dear, "Elastic and Viscous Properties of Several Soda-Silica Glasses in Annealing Range of Temperature," *Jour. Amer. Ceram. Soc.*, **20** [9] 296–304 (1937).

(*b*) N. W. Taylor, E. P. McNamara, and J. Sherman, "Elastico-Viscous Properties of Soda-Lime-Silica Glass at Temperatures near 'Transformation Point,'" *Jour. Soc. Glass Tech.*, **21** [83] 61–81 (1937); *Ceram. Abs.*, **17** [8] 273 (1938).

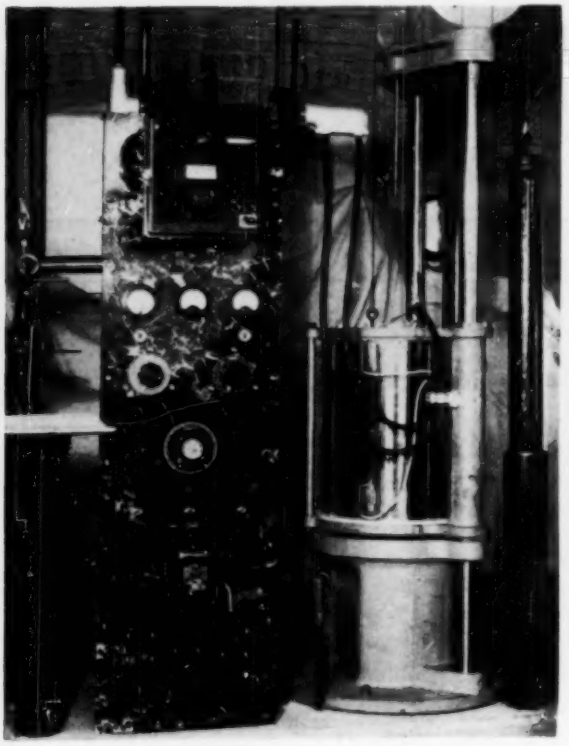


FIG. 1.—High-temperature viscometer in early stages before circular scale was added.

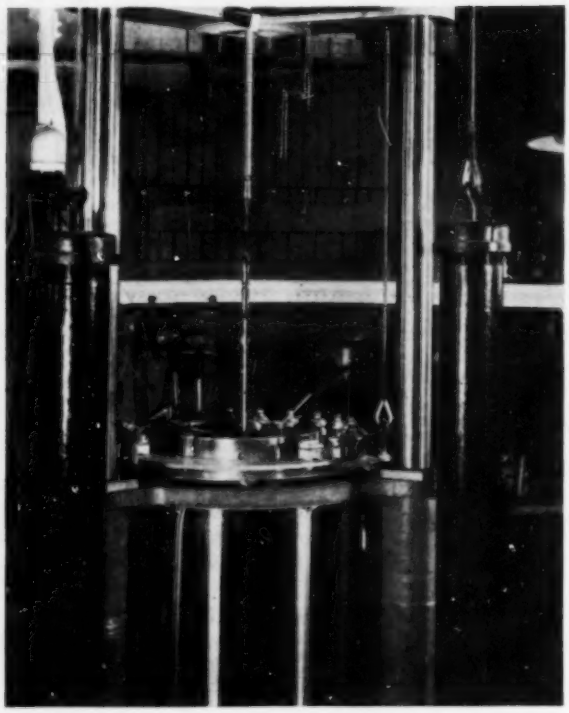


FIG. 2.—High-temperature viscometer from side showing torsion suspension, optical system, and circular scale.

II. Methods

(1) High-Temperature Viscometer (800°–1500°C.)

Before building the present equipment, a thorough search was made of the literature to determine, if possible, which type of apparatus had proved to be the most dependable as well as the most accurate. As a result of this study, it seemed clear that a concentric cylinder viscometer undoubtedly combined these two requirements better than some of the other types which have been used. This form of apparatus can be built in either of two ways, (1) the outside cylinder is rotated and the viscous drag on the inner cylinder is measured or (2) the reverse is true, the inner cylinder being rotated and the viscous drag being measured on the outside cylinder. Both types have been used at high temperatures, but it seemed that an apparatus in which the outer cylinder was rotated would offer less constructional difficulty. It is not the purpose of this paper to present at this time a résumé of the previous literature. This has recently been done by Rait,[5] who arrived at essentially the same conclusion regarding the desirability of the concentric cylinder apparatus. An instrument of this type was used in the present investigation; it is ruggedly constructed and has a minimum of parts to get out of adjustment (see Figs. 1 and 2). This last point is particularly important inasmuch as any problem involving temperature equilibrium automatically involves high labor costs. The reliability must be high in order to make a long-time program economically justifiable.

From the point of view of measurement, the work of Lillie [1(d)] appears to be the most accurate. This work follows the earlier method of Feild[6] and makes use of a concentric cylinder method in which the outer cup is revolved. The inner cylinder is suspended from a torsion wire, and the viscous drag may be measured without any of the complications arising from frictional forces. This is, in fact, the outstanding contribution of this method. Lillie, furthermore, showed that it is possible to calibrate such a device to give absolute viscosity. He designed his instrument so that the volume of the crucible or outer cylinder is much larger than the volume of the inner cylinder. A large difference in the radii of the two cylinders is not, in general, considered good rheological practice, as in such a case it is impossible to determine accurately whether or not the contained liquid will show deviations from purely viscous or Newtonian flow. The statement is often made in the literature that glass at high temperatures exhibits no plasticity. This statement is probably correct, but as far as the authors are aware there is no apparatus in existence which is capable of determining this point accurately for glass over an adequate range of shear rates. It is true, however, that a large departure from Newtonian flow could be detected in such an apparatus

[5] J. R. Rait, "Viscosity of Slags and Glasses, I–II," *Bull. Brit. Refrac. Research Assn.*, No. 50 (June, 1939); reprinted in *Trans. Brit. Ceram. Soc.*, **40** [5] 157–229 (1941); *Ceram. Abs.*, **21** [1] 16 (1942).

[6] A. L. Feild, "Method for Measuring Viscosity of Blast-Furnace Slag at High Temperature," *U. S. Bur. Mines Tech. Paper*, No. 157, 29 pp. (1916).

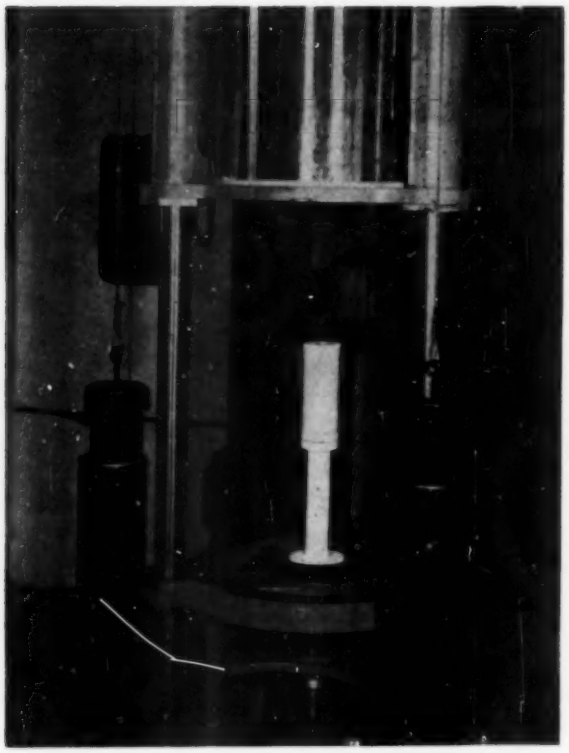


FIG. 3.—High-temperature viscometer showing revolving pedestal and crucible with furnace raised.

even though it could not be accurately evaluated. If then purely viscous flow is assumed, there is real virtue in having the outer cylinder of such a large radius compared with the inner cylinder. This advantage arises from practical considerations because it is difficult to find ceramic parts which are reproducible and also true in size and shape. The method would be considerably complicated if an outer cylinder of platinum, used as the crucible, would have to be salvaged after each determination. Sillimanite crucibles, on the other hand, can be discarded after each run and offer a saving in time and expense (see Fig. 3). The slight inconsistency occurring in the radius of these crucibles will not cause serious error with the large radius involved, nor will the small variations in centering the two cylinders cause any difficulty. The whole apparatus manipulation is therefore materially simplified. The magnitude of the errors involved is discussed in section III.

Another of Lillie's contributions to the art of measuring glass viscosities lay in the discovery that an inner cylinder with conical pointed ends gives much more highly reproducible results than do cylinders with flat ends. Such pointed cylinders yield viscosity results which are essentially independent of the depth of immersion below the surface of the liquid or the height of clearance between the bottom of the cylinder and the bottom of the crucible if these distances exceed a certain minimum.

The geometry of the apparatus* to be described is identical with that of Lillie.[1(d)] The crucibles are 6.35 cm. in inside diameter and 16.5 cm. high. This height is necessary inasmuch as the crushed sample fills the crucible completely during loading and melts down to about one half during operation. The spindle is made from a 90% platinum-10% rhodium alloy. Its radius is 0.477 cm., and its over-all length is 4.77 cm., each end of which terminates in a 90-degree cone; the cylindrical part is 3.82 cm. long. The spindle is attached to a sillimanite rod by means of a 90% platinum-10% rhodium rod, 1.6 mm. in diameter. The ceramic rod serves both as a support for the spindle and as an insulator for the main temperature-measuring thermocouple. The rod terminates in a small chuck by which it is attached to the torsion wire. The sillimanite crucible is mounted on an Alundum pedestal, which is rotated by means of a $^1/_6$-h.p. synchronous motor. The motor is coupled to the pedestal through a gearbox and pulley arrangement so that three speeds of rotation can be maintained merely by changing the driving belt from one pulley to the next. This arrangement gives speeds of revolution whose periods in seconds are 32.47, 20.65, and 12.00. These periods have been carefully checked from time to time and have never varied by more than 0.01 or 0.02 point. The calibration is made simply by measuring the time for 100 revolutions.

The torsion wires from which the spindle is suspended are made from 3-in. lengths of steel piano wire of several different gauges. Except for some of the heavier of these wires, they have proved to be remarkably stable in operation. The torsional characteristics can be accurately determined by timing the period of oscillation when loaded with each of several weights. All wires are shielded from direct radiation from the furnace by a small tinfoil shield. The torque constants in dyne centimeters per radian of twist have been found to be 2.299×10^4, 6.008×10^4, 1.252×10^5, 3.533×10^5, and 6.568×10^5 for the five suspensions most frequently used.

The original furnace described by Lillie used a molybdenum winding in an inert atmosphere. In his more recent work, this furnace was discarded in favor of a simply wound 90% platinum-10% rhodium coil on a sillimanite tube covered with Alundum cement. Recent studies† indicate that furnace windings of very pure platinum have an appreciably longer life than do those of platinum-rhodium. Although this practice is at variance with published ideas of furnace construction, the results seemed sufficiently clear to warrant the use of pure platinum in place of the alloy. Because of the larger temperature coefficient of resistivity of pure platinum, the heating current must be applied relatively slowly in order to prevent overloading the circuit. This slow heating has previously been considered a drawback in furnace construction and is the main reason why platinum-rhodium has hitherto been used. An automatic mechanical relay device has been constructed which makes it possible to advance the autotransformer

* The sillimanite crucibles and furnace cores have been obtained from the Corning molds through the courtesy of the Corning Glass Works.

† These studies were carried out by the J. Bishop Company, Malvern, Pa.

automatically according to some predetermined schedule. The voltage is thus automatically increased a set amount every thirty minutes, and no time is lost in bringing the furnace up to temperature. It has, in fact, even proved feasible to start the furnace in the morning and have it balanced at 2500°F. seven hours later. The first point may thus be obtained the first day. The normal procedure, however, is to heat up the furnace somewhat more slowly than this.

The surface of the sillimanite furnace core is heavily scored in a helix to take the winding. The 0.050-in. diameter platinum, purposely made several feet too long, is wound around a mandrel into a coil approximately 1/4 in. in diameter and the coil is stretched exactly to the length of the helix. A heavier density of wire per inch of helix is thus secured than would have been possible if the wire had been simply laid into the groove. This coil is then imbedded in Alundum cement. The preliminary heating of the coil provides sufficient heat to set the cement. The sillimanite core with the winding is set in Alundum annular rings at both ends of the vertical furnace. These rings, in turn, are supported by cement-asbestos composition disks, and an extra steel annular ring supports the whole furnace. The core is surrounded with 5 in. of diatomaceous earth, and three concentric 26-gauge stainless steel casings, spaced at roughly 3/8 in. one from the other, surround the diatomaceous earth. This insulation has been remarkably effective in cutting down radiation from the sides of the furnace. When the glass reaches 2500°F., the hand can barely detect any radiation within 1/2 in. from the outermost steel casing. The radiation from the ends of the furnace, of course, is somewhat greater but is controlled by auxiliary coils, one above and one below the glass. At 2500°F., the upper coil takes approximately 160 volt-amp. and the lower coil 20 volt-amp. in order to maintain temperature equilibrium over the volume of the glass. The main heater takes approximately 1300 volt-amp. The upper coil is supported by a cylindrical plug which just fits into the furnace core from the top. The bottom coil is inserted in the middle of the pedestal and is wound on a vertical sillimanite tube which is inserted into the pedestal. This coil was so wound in order to minimize inductive effects resulting from the on and off current in the external heating coil. After a crucible containing the sample has been mounted on the bottom pedestal and carefully lined up and made vertical, the furnace is brought down over the glass and pedestal, and diatomaceous earth is poured around the outside of the pedestal to act as a seal. That this seal is effective is shown by the relatively low amount of power necessary to maintain constancy of temperature in the bottom coil. The current is maintained in the bottom coil during the rotation of the cylinder by means of slip rings.

Thermocouples are inserted in the space between the crucible and the main core, up into the bottom pedestal, and down into the top plug. These last two thermocouples are balanced by hand against the main measuring couple. The latter is inserted through the sillimanite tube which connects the platinum spindle and the torsion wire. The main measuring thermocouple has its measuring end protected by a small platinum shield from all radiation except that directly emanating from the glass and is placed approximately 1 cm. above glass level. The controlling thermocouples are platinum-platinum 10% rhodium and are permanently placed although they are designed so that they may be changed with a minimum of difficulty. The main measuring couple was calibrated at the Bureau of Standards and is changed after every eight runs. These couples make it possible to balance the temperature above and below the glass to within a few microvolts of the temperature inside the glass and thus insure that the whole crucible is in a constant-temperature zone. Final viscosity measurements are made one hour after equilibrium has been attained and then only after prolonged stirring of the glass by means of the inner spindle.

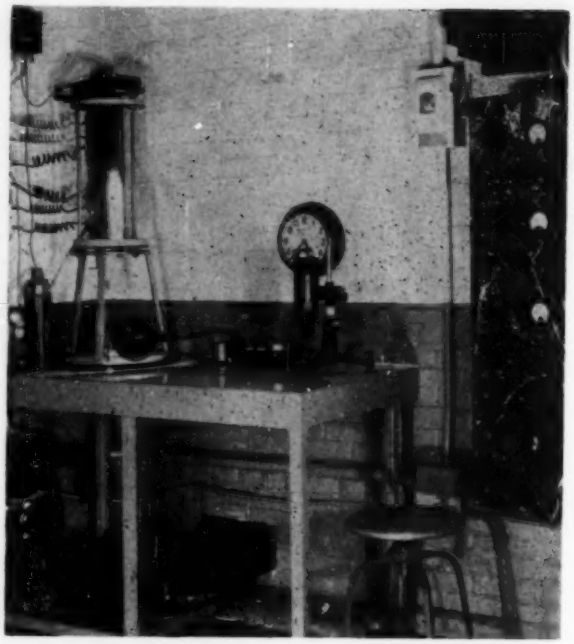


FIG. 4.—Low-temperature viscometer showing automatic temperature control apparatus beneath table.

The voltage supply at the furnace is first smoothed to within 1% by means of a 3 kv.-amp. Sola transformer. The current for the main winding and the two auxiliary windings is hand set by means of an autotransformer. Temperature in the main winding is automatically controlled after the current has been set by means of a Tagliabue Celectray temperature controller. This combination has worked satisfactorily, but to use the controller automatically at the high temperatures an auxiliary small resistance must be plugged in and out of the circuit instead of using on and off control of the entire current. This necessity arises from the fact that the thermocouple system behaves erratically when the full on and off operation is used above 2200°F.

(2) Low-Temperature Viscometer (450°–650°C.)

As stated previously, a different type of apparatus is necessary when measuring extremely high viscosities from that used to measure lower viscosities. The simplest and most direct means for carrying out viscosity measurements in the range between 10^{10} and 10^{16} poise is by means of a fiber-elongation method. Measurements by this method have been carried out by many people but most intensively by Taylor and his students[4] with the apparatus previously designed by Norton[3] (see Fig. 4).

The furnace has the central 12 in. of the fiber cavity at constant temperature, which is accomplished first by setting the approximate temperature of the furnace in the center coil and increasing the voltage on auxiliary end coils until they match the central temperature. A Variac control was used for this purpose. Balance was then maintained between the end and middle coils by means of a simple photoelectric setup, in which the differential from a thermocouple is applied directly across a sensitive galvanometer, which in turn reflects a light beam across the photocell. This photocell controls a relay which plugs an auxiliary resistance in or out of the end circuits. The temperature of the central part of the furnace is maintained by means of the lever arrangement described by Norton.[3] This arrangement uses the expansion and contraction of the furnace core as an accentuating mechanism through a 40- to 1-lever to operate a series resistance. This furnace is likewise run from a Sola constant voltage transformer.

In making a determination, glass fibers are first drawn by hand from the sample and cut into lengths about 10 in. long. These fibers range from 0.5 to 1 mm. in diameter. The fiber has a small glass bead fused on one end and is hung from a stirrup, which in turn is suspended from the top of the furnace. A second stirrup is then suspended from the bottom of the fiber by means of a bead fused on the lower end of the glass. A third stirrup for carrying the weights is fastened to the second stirrup by means of a wire and spherically seated links. The total weight of the bottom wire and stirrup assembly is exactly 10 gm.

(3) Softening Point Furnace

The temperature at which the viscosity is 4.5×10^7 poise is measured on a small softening-point furnace. The design, construction, and operation of such a furnace have been described by Littleton.[7]

The measured values of the softening point may be compared with the value of log viscosity equal to 7.65 as calculated from the Fulcher[8] equation. The constants of the equation were obtained by a least squares calculation, using the measured viscosity points. The comparison is given in Table I.

The differences between measured and calculated points are predominantly negative, probably indicating that the primary standard is about two degrees low.

Table I

Measured vs. Least Square Calculated Softening Points (°C.)

Glass No.	Measured value	Calc. temp. for log η = 7.65	Measured − calculated
2	711	714	−3
10	732	731	+1
11	727	727	0
34	691	690	+1
35	698	702	−4
36	692	694	−2
37	696	699	−3
38	717	718	−1
39	712	712	0
40	719	722	−3
51	709	711	−2
56	697	703	−6
57	725	729	−4
308	702	703	−1
312	717	720	−3
330	674	675	−1

Inasmuch as this was initially furnished with an estimated error of ±2°C., the check is seen to be satisfactory.

III. Calculation of Results

(1) High-Temperature Viscometer

There are two methods in use by which the viscosity at high temperatures can be calculated. The first of these consists in rotating the outer crucible at a constant speed and measuring the angular deflection of the inner cylinder by means of a mirror and scale arrangement. This method is used when the viscosity is less than 50,000 poise. For higher viscosities, it is impossible to find torsion wires which are heavy enough and which obey Hooke's law sufficiently accurately to make them satisfactory as suspensions. In this case, the so-called aperiodic method is used. In this method, the outer crucible is turned slowly by hand until the deflection shown on the scale is greater than 30 cm. from the initial position of rest. Because of the extreme viscosity of the liquid glass, the spindle returns to its zero position very slowly. The time of transit of the light beam across the scale is taken between several sets of points, in this case between deflections of 30 and 20 cm. and of 15 and 5 cm. The deflection is made in both directions, and it is important that the rest position of the inside spindle be such that the position of the light beam registers accurately on zero under no torque. It is thus possible to extend the viscosity range up to approximately 3×10^6 or 3 million poise. It is the extension of the viscosity range by this aperiodic method which makes an apparatus of this type so valuable for measuring viscosities. There are, in fact, very few other methods by which it would be possible, as it is in this case, to measure viscosities from the extreme low range of 0.1 to several million poise.

The method used for calculating the results in the periodic case is well known and can be shown by equation (1).

$$\eta = \frac{KDt}{4\pi CdLE} = \text{const.} \times \frac{Dt}{L} \qquad (1)$$

η = viscosity (poise).

[7] J. T. Littleton, Jr., "Method for Measuring Softening Temperature of Glasses," *Jour. Amer. Ceram. Soc.*, **10** [4] 259–63 (1927).

[8] G. S. Fulcher, "Analysis of Recent Measurements of Viscosity of Glasses," *ibid.*, **8** [6] 339–55 (1925).

D = scale of deflection (cm.).
t = time of revolution of outer crucible (seconds).
$C = \frac{4\pi(R_1)^2(R_2)^2}{(R_2)^2 - (R_1)^2}$
R_1 = crucible radius (cm.).
R_2 = spindle radius (cm.).

For the present crucibles, the average inside diameter varies from 6.342 to 6.457 cm. Greater variations presumably can also occur. Because the radius of the platinum spindle is 0.477 cm. at room temperature, a change in the external diameter from 6.198 to 3.604 cm. will cause a change in the apparatus consant C from 2.928 to 2.920. The average of this constant is 2.924, which bears out the contention previously expressed that small variations in the diameter of the outside crucible have relatively little effect on the calculated viscosity. The extreme variation in diameter from 6.2 to 6.6 cm. changes the viscosity only by $\pm 0.13\%$. The actual variation in diameter is seen to be much less.

d = scale distance from torsion wire (cm.); a circular scale at a radius of 99 cm. has been used; an error of 1 mm. here will cause an error of $\pm$ 0.1%.
L = effective spindle length, determined by calibration to be equal to 4.53 cm.; may be checked to within 1%; a discussion of this calibration is given later.
E = volume temperature expansion factor for spindle; this factor is equal to 1.04 for platinum at 1200° to 1300°C., which is the middle of the measured range. The error in this term is slightly under 1%.
K = torque constant of spring (dyne cm./radian of twist).

The numerical factor, $4\pi CdE$, is found to equal 3783 for this apparatus at elevated temperatures; it is 4% lower at room temperature because E then is equal to 1.

For a spindle of the type described, Lillie[1(c)] was able to derive an effective spindle length of 4.53 cm. by using a method which essentially makes the apparatus capable of giving absolute results and which he has fully described. He also showed that this factor was constant for liquids whose viscosities range from 5 to 3500 poise. Ever since the initial work of Washburn and Shelton,[9] there has been some doubt about the constancy of calibration of concentric cylinder viscometers over a wide range of viscosities. This lack of constancy, which has not been found by other investigators, is unvuestionably spurious and was probably caused by a skin formation over the surface of the glucose used as a calibrating liquid.[10(a)] Lillie[1(c)] also used glucose as a standard medium. In recent years, commercial development of the polyisobutylenes has placed in the hands of rheologists an important new viscosity calibrating liquid. Aside from being available over a wide viscosity range, its temperature coefficient of viscosity is very small. Ferry and Parks[11] have reported values of $d(\log \eta)/d(1/T)$ for polyisobutylene as low as 0.3 of those found for glucose. It appeared to be of interest to repeat the calibration *in situ* at room temperature at the higher viscosities in this laboratory.

A Vistanex sample submitted to the Bureau of Standards was reported to have a viscosity of 2063 $\pm$ 0.2% poise at 20°C. and 732.6 $\pm$ 0.2% poise at 30°C. The sample was then run in this laboratory at 22°C. and at 26°C. These temperatures were selected as being slightly above room temperature and were maintained by the Celectray controller with a Chromel-Alumel couple in exactly the same way that it is used at elevated temperatures. The temperatures were measured by means of a copper constantan couple calibrated at the Bureau of Standards. In this calibration, it was assumed that log η for Vistanex varies linearly with $1/T$(°K.) over the short (10°C.) range of interest.

The average of a number of determinations made in this laboratory gave an effective spindle length, L, of 4.57 cm., which is within 1% of the value 4.53 inherent in Lillie's calculation. In view of the fact that the Lillie calibration was made on several liquids over a wide viscosity range, his value has been assumed for all calculations used in this paper. It has been possible to show, moreover, that the Lillie calibration using glucose is correct. Inasmuch as there is no reason to suspect his calibration obtained by the use of castor oil and because it also checks the 4.53 figure, further evidence has now been obtained that the original Washburn work was in error. This same error has also been found and discussed by Proctor and Douglas[10(a)] and inferred by Babcock.[10(b)] It cannot be assumed, however, that all glucose calibrations are incorrect.

In the aperiodic method, the viscosity is calculated from formula (2), which was derived by Lillie.[1(a,b)]

$$\eta = \frac{0.4343K}{ECL \log \frac{\theta_1}{\theta_2}} (T_2 - T_1) \qquad (2)$$

$T_2 - T_1$ = time (seconds for spindle to return from angle θ_2 to angle θ_1).
Log θ_1/θ_2 for distance between 30 and 20 cm. on scale = 1.689 (in this particular case).
Log θ_1/θ_2 for scale distance between 15 and 5 cm. = 0.4736.
K, E, C, and L are same as those in equation (1).

Thus for suspension number 3, which has a torsion constant equal to 1.252×10^5, the viscosity will be given by $8.333 \times 10^3 \times T_2 - T_1$ when timing between the 15- and 5-cm. marks and by $2.338 \times 10^4 \times T_2 - T_1$ between the 30- and 20-cm. marks. The evaluation of the viscosity then is extremely simple for it is necessary only to multiply this constant by the time required. The periodic method is equally simple because it is possible again to build up a table of constants for each calibrated torsion wire at each speed and then to multiply a specific constant times the deflection as noted on the scale.

The degree of reproducibility of the measurements made by this apparatus is high (see Table II). Three

[9] E. W. Washburn and G. R. Shelton, "Viscosities and Surface Tensions of Soda-Lime-Silica Glasses at High Temperatures: I, Viscosities of Glasses at High Temperatures," *Univ. Ill. Eng. Expt. Station Bull.*, No. 140, pp. 8–50 (April 14, 1924); *Ceram. Abs.*, **3** [12] 336–44 (1924).

[10] (*a*) R. F. Proctor and R. W. Douglas, "Measurement of Viscosity of Glass at High Temperatures by Rotating Cylinder Viscometer," *Jour. Soc. Glass Tech.*, **13** [51] 194–213 (1929); *Ceram. Abs.*, **9** [5] 340 (1930).
(*b*) C. L. Babcock, "Viscosity and Electrical Conductivity of Molten Glasses," *Jour. Amer. Ceram. Soc.*, **17** [11] 329–42 (1934).

[11] J. D. Ferry and G. S. Parks, "Viscous Properties of Polyisobutylene," *Physics*, **6**, 356–62 (1935).

TABLE II

DEGREE OF REPRODUCIBILITY OF APPARATUS

Log η =	2.5	3	4	5	6	Softening point
	Degree of reproducibility of complete apparatus					
Original run (°C.)	1348	1228	1052	928	836	
1st rerun (°C.)	1353	1232	1053	928	835	
2d rerun (°C.)	1346	1227	1051	927	835	
Avg. (°C.)	1349 ± 4	1229 ± 3	1052 ± 1	928 ± 1	835 ± 1	
	Degree of reproducibility between two separate pieces of apparatus					
Corning values (°C.)	1311	1197	1032	916	831	733
Armstrong values (°C.)	1324	1204	1034	917	832	733

TABLE III

GLASS COMPOSITION (%)

(All Flint Glasses Except Where Noted)

Glass No.	Description†	Na_2O	K_2O	CaO	MgO	Al_2O_3	BaO	B_2O_3	Fe_2O_3	SiO_2
2		14.3		7.33	4.04	2.74	0.08	0.47	0.10	71.0
10	Amber	11.9	1.18	10.6	0.62	2.73	.93	.89	.14	70.4
11		12.6	0.98	6.01	4.02	2.58	.58	.85	.06	71.8
34	D	17.2		5.02	3.49	1.68	.05	.86	.06	71.6
35	C	15.9		9.16	0.52	1.58	.26	.83	.06	71.7
36	F	15.7	0.46	5.58	3.35	1.05	.24	.46	.07	73.3
37	E	16.4		5.35	3.47	1.60	.08	.46	.07	72.6
38	H	15.3		5.43	4.07	1.14	.42	.33	.06	73.3
39	I	15.3		5.92	4.00	2.04	.42	.28	.06	72.0
40	G	14.5		6.76	4.38	1.43	.51	.00	.06	72.1
51*	Emerald	14.9	0.29	10.7	0.59	0.88	.62	.54	.07	71.0
56	A	16.0		4.87	3.42	1.08	.75	.75	.06	73.1
57	B	12.5	2.19	6.32	4.29	3.66	.58	.86	.06	69.4
308	Amber	15.4	0.27	9.84	0.70	1.11	.59	.65	.13	71.4
312		14.1	0.29	7.28	4.82	1.44	.44	.00	.07	71.7
330	Pot glass	17.7	0.89	5.60	4.07	1.61	.16	.76	.10	69.1

* Glass No. 51 contains +0.21 Cr_2O_3.
† Letters D, C, F, E, H, I, G, A, and B denote glasses evaluated by Owens and Emanuel see footnote 13, p. 137.

separate runs made by two different observers over a period of more than a year have been fitted to equation (3) by a least squares calculation.

$$\text{Log } \eta = -A + \frac{B}{T - T_0} \tag{3}$$

The three constants A, B, and T_0 were thus evaluated, and the temperatures corresponding to various values of log η were calculated. An equation of this type was first given by Fulcher.[8]

Table II also shows a similar calculation for a glass viscosity run both at the Corning Glass Works and at this laboratory. The agreement is satisfactory.

(2) Low-Temperature Viscometer

The formula for determining the viscosity by this method is well known (see equation (4)). A derivation is given by Lewis, Squires, and Broughton.[12]

$$\eta = \frac{Fl}{3A\dfrac{dl}{dt}} \tag{4}$$

F = extending force (dynes).
l = fiber length (cm.).
A = fiber area (sq. cm.).
dl/dt = elongation rate (cm./second).

[12] W. K. Lewis, Lombard Squires, and Geoffrey Broughton, Industrial Chemistry of Colloidal and Amorphous Materials, p. 24, Macmillan Co., New York, 1942. 540 pp.

It is convenient to make two substitutions for ease in manipulation. These are to replace the area by the volume (the volume remains constant throughout a determination; the area does not) and to express dl/dt in centimeters per minute. With these changes, it is easy to derive equation (5).

$$\eta = \frac{20mgl^2}{V\,dl/dt} \tag{5}$$

m = appended mass (gm).

By separating the variables in this equation and putting in the general limits, $l = L_0$ when $t = T_0$ and $l = L$ when $t = T$, the equation can be integrated and equation (6) is obtained. Instead of measuring the

$$\eta = 19{,}600\,\frac{m}{V}\,\frac{L_0L_1}{L_1 - L_0}\,(T_1 - T_0) \tag{6}$$

diameter of the fiber at the point of measurement, it is thus only necessary to measure the volume at room temperature and to correct this volume by means of the coefficient of expansion of the glass. In the normal procedure, the volume of the fiber is measured both before and after the run and the average of the two readings is taken. This measurement is made by calipering the diameter of the fiber at the top, middle, and bottom at any one diameter and at right angles to this diameter. The fibers have been carefully selected beforehand for constancy of diameter and "roundness." When viscosities are to be measured below the anneal-

TABLE IV

CONSTANTS FOR FULCHER EQUATION* AND VISCOSITY TEMPERATURE RESULTS FOR GLASSES CALCULATED BY LEAST SQUARES METHOD

Glass No.	*B*	*A*	T_0 (°C.)	Log η 2.5	3	4	5	6	Softening point 7.65	Annealing point 13.37	Strain point 14.60
2	4690	1.769	216.2	1316†	1201†	1030†	910†	821†	714†	526†	503†
10	4238	1.578	271.7	1311	1197	1032	916	831	731	555	534
11	4478	1.540	241.8	1350	1228	1050	927	836	727	542	520
34	4197	1.448	229.0	1293	1173	1000	881	793	690	512	491
35	4237	1.659	246.8	1267	1157	997	884	801	702	529	507
36	4577	1.635	200.9	1309	1189	1014	892	801	694	506	483
37	4528	1.589	209.1	1317	1197	1020	897	807	699	512	489
38	4653	1.574	214.0	1347	1232	1050	923	829	718	525	502
39	4662	1.680	216.3	1332	1212	1037	914	823	712	526	503
40	4747	1.776	218.4	1329	1212	1040	919	829	722	532	508
51	4092	1.637	270.7	1261	1154	998	888	807	711	543	521
56	4635	1.664	205.2	1319	1200	1025	902	811	703	514	490
57	4482	1.559	242.8	1348	1226	1050	927	836	729	543	520
308	4057	1.533	261.3	1268	1157	996	883	801	703	533	513
312	4730	1.851	221.7	1326	1204	1028	907	819	715	538	513
330	4229	1.631	219.0	1219	1132	970	857	773	675	501	480

* See equation (3), p. 135.
† Column in °C.

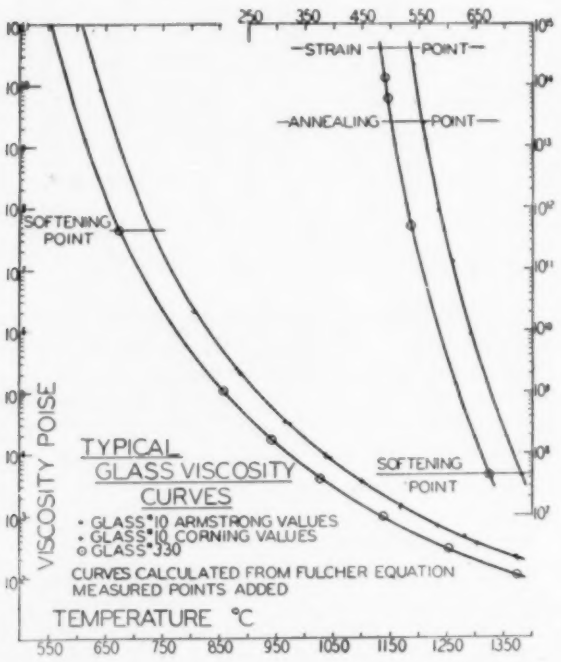
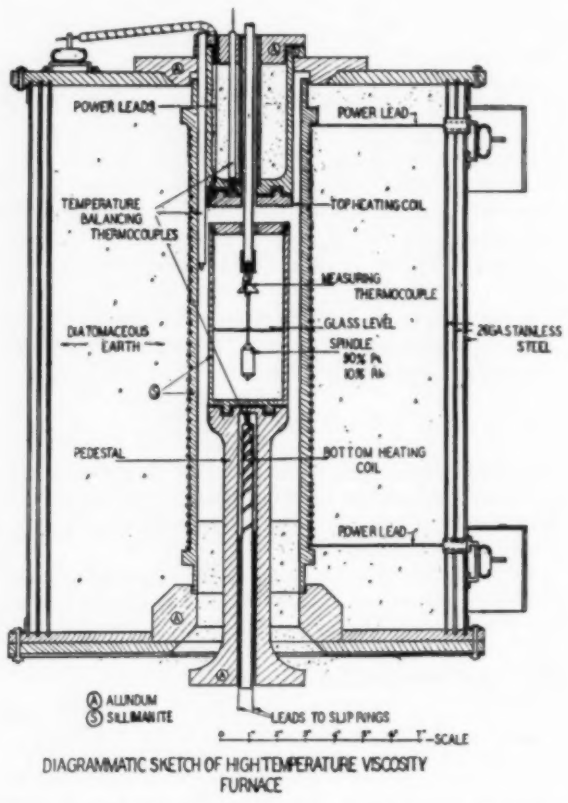


FIG. 5.—Maximum and minimum viscosity curves.



DIAGRAMMATIC SKETCH OF HIGH TEMPERATURE VISCOSITY FURNACE

FIG. 6.—High-temperature viscosity furnace (diagrammatic sketch).

ing point, that is, 2.5×10^{13} poise, only those fibers which have been carefully annealed should be used. Failure to make this selection will lead to excessive time of measurement and erroneous results. The reasons for this are well understood and have been adequately described in the literature.

In the present determination, the limiting factor in the accuracy is probably the $\pm 1\%$ error in the volume determination and the inaccuracy of $\pm 1°$ in the temperature measurement. The length can be measured easily to $\pm 0.2\%$. Because the determination consists in measuring the average rate of elongation while the fiber is elongating approximately 1 cm. in length, for each of three different weights, the reproducibility of the apparatus is high in spite of the fact that temperature coefficients of viscosity in this range are enormous. Figures to show this result are not given here but are similar to those shown by Taylor.[4]

Appendix: Experimental Results

Temp. (°C.)	Log η
Glass No. 2	
510	14.217
523	13.625
541	12.754
540	12.775
539	12.824
566	11.701
586	10.925
601	10.380
711	7.653*
862	5.524
931	4.815
1043	3.913
1167	3.165
1275	2.677
1358	2.331
Glass No. 10	
538	14.338
555	13.408
567	12.787
585	11.961
608	11.132
641	9.952
732	7.653*
885	5.383
972	4.485
1045	3.922
1168	3.167
1281	2.656
1370	2.320
Glass No. 11	
529	14.046
568	12.156
589	11.389
608	10.745
727	7.653*
865	5.724
942	4.892
1032	4.146
1144	3.447
1255	2.881
1365	2.431
Glass No. 34	
500	13.957
542	12.006
543	11.993
564	11.078
601	9.801
691	7.653*
846	5.340
861	5.245
943	4.438
1026	3.820
1139	3.169
1251	2.647
1308	2.425

Temp. (°C.)	Log η
Glass No. 35	
523	13.843
543	12.679
567	11.545
602	10.220
698	7.653*
863	5.220
944	4.405
1029	3.752
1136	3.114
1250	2.585
1305	2.368
Glass No. 36	
500	13.614
543	11.818
564	11.034
601	9.760
692	7.653*
864	5.293
944	4.518
1026	3.909
1137	3.252
1247	2.737
1318	2.463
Glass No. 37	
501	13.858
543	12.046
567	11.130
602	9.927
696	7.653*
861	5.384
940	4.603
1021	3.982
1133	3.312
1249	2.766
1311	2.518
Glass No. 38	
509	14.176
524	13.415
541	12.679
568	11.653
602	10.405
717	7.653*
863	5.631
939	4.856
940	4.841
1023	4.175
1134	3.480
1245	2.930
1304	2.684

Temp. (°C.)	Log η
Glass No. 39	
506	14.412
523	13.489
542	12.727
568	11.604
602	10.354
712	7.653*
861	5.577
941	4.772
944	4.735
1022	4.107
1135	3.400
1246	2.852
1361	2.393
Glass No. 40	
510	14.543
523	13.798
542	12.938
566	11.933
601	10.619
719	7.653*
862	5.621
943	4.692
1034	4.103
1137	3.382
1248	2.831
1362	2.368
Glass No. 51	
562	12.080
581	11.618
616	10.246
709	7.653*
864	5.312
944	4.467
1029	3.763
1143	3.065
1255	2.536
1312	2.308
Glass No. 56	
514	13.377
521	13.064
571	11.029
697	7.653*
862	5.405
941	4.643
940	4.636
1029	3.955
1136	3.318
1255	2.761
1316	2.515

Temp. (°C.)	Log η
Glass No. 57	
580	11.779
618	10.392
725	7.653*
835	6.076
939	4.900
1030	4.148
1142	3.428
1255	2.865
1373	2.393
Glass No. 308	
562	11.963
574	11.412
615	10.023
702	7.653*
863	5.273
943	4.418
1029	3.741
1144	3.058
1265	2.507
1370	2.132
Glass No. 312	
565	11.982
578	11.390
615	10.227
717	7.653*
863	5.561
943	4.694
1026	4.016
1140	3.301
1261	2.712
1310	2.504
Glass No. 330	
489	14.012
495	13.780
535	11.704
674	7.653*
857	5.022
941	4.237
1027	3.597
1137	2.982
1253	2.459
1373	2.033

* Softening points.

IV. Viscosity Results

The glasses whose viscosities are being reported were bought on the open market and were carefully analyzed according to the standard laboratory methods. The results are listed in Table III. In several cases, the glasses were reanalyzed at a later date, and the results were averaged wherever more than one analysis was available. Several of the analyses were carried out on glasses obtained from the same lot and at the same time as those described in another paper from this laboratory; these glasses are identified by the inclusion of a capital letter which was used to designate them in the report by Owens and Emanuel.[13] The identification numbers have no significance. The boron analyses as

[13] J. S. Owens and E. C. Emanuel, "Effect of Storage Conditions on Weathering of Commercial Glass Containers," *Jour. Amer. Ceram. Soc.*, **25** [Sept. 1, No. 13] 359–71 (1942).

given may be slightly high; glasses Nos. 40 and 312 have been checked spectroscopically for boron. Check analyses run in several other laboratories in an effort to substantiate these boron results have shown that present methods for this element are not entirely reliable.

In determining the viscosities, it is impossible to measure every glass at a common set of temperatures. This means that it is difficult to compare results between various glasses. Each glass, therefore, has been fitted by least squares methods to equation (3) and the three constants, A, B, and T_0, have been calculated.

$$\text{Log } \eta = -A + \frac{B}{T - T_0} \qquad (3)$$

The fit between experiment and empirical formula is within 0.5%. There can be no question but that this equation gives a true and accurate representation of the connection between viscosity and temperature for soda-lime glasses when measured by the method described. It should be pointed out that this includes not only calcite but also dolomitic glasses. Several other types of three- and four-constant equations were tried without success (equations (7) and (8)).

$$\text{Log } \eta = -A + \frac{B}{T} + \frac{C}{T^2} + \frac{D}{T^3} \qquad (7)$$

$$\text{Log } \eta = A - B \log T - \frac{C}{T} + \frac{D}{T^2} \qquad (8)$$

Equations (7) and (8), for example, cannot even be considered as empirical equations because the fit is too bad. The Waterton equation,[14] because of its form, does not lend itself easily to a least squares calculation. The success of the simple Fulcher equation is surprising, particularly in view of the fact that the more elaborate equations give so poor a fit.

The constants for the Fulcher equation and the temperatures calculated from them at several constant log viscosities are given in Table IV. Results are shown in Fig. 5, and the experimental results are listed in the Appendix.

In Table IV, the columns marked softening, annealing, and strain points represent temperatures calculated for log viscosity, 7.65, 13.37 and 14.60, respectively, from data measured at constant temperature by the method already described. Like the softening points, the annealing points obtained in this way check the results obtained in other laboratories by the normal methods very closely. The agreement at the strain point is open to question, however, as the error in this determination from any one laboratory is probably ±20°. It can be shown, however, that the log η versus T (°K.) curves for these glasses are essentially straight lines, at least between 10^{13} and 10^{15} poise. Marked deviations from straight lines, such as are sometimes found at the strain point, are undoubtedly the result of the strain-point apparatus or some other cause and do not represent a property of the glass itself.

Acknowledgment

The authors acknowledge with thanks several helpful conversations with H. R. Lillie and Nelson W. Taylor on the subject matter of this paper. Much of the engineering of the apparatus was worked out with C. C. Schrader of this laboratory. The two furnaces were constructed by the H. E. Trent Company of Philadelphia according to specifications of the writers. Figure 6 is a line drawing from one of their working drawings and is reproduced with their permission.

Armstrong Cork Company
Lancaster, Pennsylvania

[14] S. C. Waterton, "Viscous-Temperature Relationship and Some Inferences on Nature of Molten and Plastic Glass," *Jour. Soc. Glass Tech.*, **16** [62] 244–53 (1932); *Ceram. Abs.*, **11** [12] 609 (1932).

ANALYSIS OF CORDS AND STONES*

By G. J. Zarbo, H. J. Hunt, and D. C. Smith

Abstract

A method is described for the separation of cords and stones from the surrounding glass, and procedures are given for the semimicro-determination of silica and alumina. The apparatus is illustrated. Analytical results by full-scale methods and semimicro-methods are given. The methods of semimicro-analysis are shown to be rapid and accurate.

I. Introduction

When stones or cords occur during the production of glass, the identification of the contaminating material is highly desirable. The quickest method, of course, is a petrographic examination, which includes the determination of the refractive index and other optical characteristics of any crystalline material present. Chemical analysis, however, is the only means of identification if no crystals are present. Even when petrographic analysis is possible, it is sometimes desirable to check the findings by means of a chemical analysis, either on the crystals themselves or on the entire inclusion.

The inclusion is sometimes large enough to permit a full-scale analysis. When the available samples are too small for analysis by ordinary methods, it is necessary either to analyze a number of lumps collectively or to investigate a single lump by semimicro-methods.

The semimicro-method, applied to a single lump, possesses several advantages.

* Presented at the Glass Division Autumn Meeting, Absecon, N. J., September 19, 1942. Received December 16, 1943.

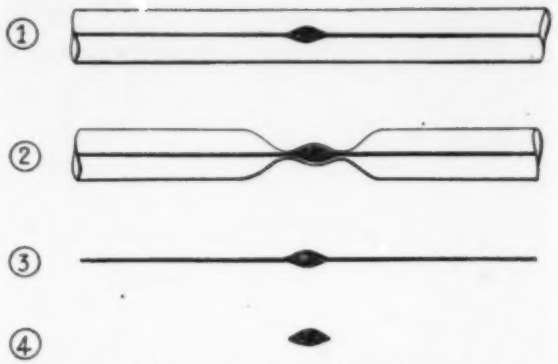


FIG. 1.—Steps involved in separation of lumps in glass.

(1) It is often impossible to be certain that all of a large number of lumps are caused by the same conditions in the furnace.

(2) The preparation of a large number of samples for analysis requires a considerable amount of care and time. Information can be obtained more quickly by working from a single lump.

(3) The actual determination of alumina on a semimicro-scale requires considerably less time than the conventional method. As far as silica determinations are concerned, the writers have found little difference in time required for analysis by macromethods and micromethods.

(4) In the semimicro-method, the analysis can be made on samples weighing as little as 60 mg. This means that the analysis can be restricted to the center portion of even a small stone or cord, with most of the surrounding glass stripped away. Results are therefore indicative of the true composition of the inclusion as distinguished from the composition of the matrix glass.

II. Technique of Separating Inclusions

The success of this method of cord analysis depends on the development of a satisfactory technique for the physical separation of the inclusion from the glass. For this reason, the preparation of the samples will be discussed in detail.

There are two main types of inclusions. (1) Some inclusions consist of lumps of glass, either with or without opaque centers, having considerably higher viscosity than the matrix glass. These lumps are easily separated by heating over a blast lamp. Figure 1 shows the steps involved in making such a separation. The glass is heated cherry-red, withdrawn from the flame, and pulled lengthwise, whereupon the matrix glass being softer tends to pull away from the lump. It is then reheated, and the operation is repeated several times until the bulk of the matrix glass has been removed. (2) A second type of inclusion consists of cords with a composition so close to that of the surrounding glass that the pulling operations described for type (1) are not successful. This type of cord is probably the more common and consists of a faint streak or stria. The cord, in this case, can be cut out by using a silicon carbide wheel and finishing on a small grinder of the type used in dental laboratories. Figure 2 shows the principal steps in preparing this type of cord. After the preliminary cutting has been completed, the sample is transferred to the fine grinder and the progress of removing the matrix glass is carefully followed by observation under a low-power binocular microscope with the sample immersed in xylene.

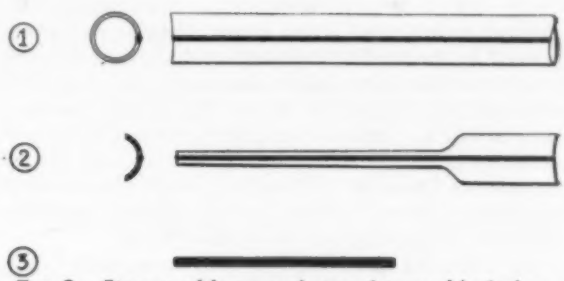


FIG. 2.—Steps used in preparing cord type of inclusion.

After the sample is prepared by either of these methods of separation, it is ground to pass a U. S. No. 100 screen and is ready for analysis. The determination of silica and alumina has usually proved of most assistance in locating the source of trouble, and the results described in this paper include only the determination of these two constituents. The methods of determination for full-size samples are well known and need no repetition here. For semimicro-determinations, no standard methods were available, and it was necessary to develop suitable procedures, which are described in section III.

III. Semimicro-Determination of Silica

(1) Weigh 50 mg. of powdered sample to the nearest 0.01 mg. in a tared platinum crucible, add 100 mg. of Na_2CO_3, and mix by rotating crucible.

(2) Cover crucible and heat carefully for a few minutes; then increase flame and heat until fusion is complete.

(3) Cool; wash any particles from lid into crucible with approximately 1 ml. of water; digest on steam bath to disintegrate melt.

(4) Cover crucible with pear-shaped cover glass; very carefully add 1 ml. of 1:1 HCl; digest on steam bath until effervescence ceases, and wash cover glass with water; break any lumps remaining with a clean platinum rod. If boron is present, add 0.5 ml. of CH_3OH, and evaporate dry on steam bath; if amount of boron is greater than 5%, repeat treatment with CH_3OH and evaporate very carefully to dryness.

(5) Drench residue with 0.5 ml. of HCl (concentrated); add 5 ml. of hot water; digest on steam bath for 5 minutes.

(6) Filter with microfiltering apparatus into a clean platinum crucible; wash with five 0.5-ml. portions of hot HCl (2:98) and two 0.5-ml. portions of hot water; mix thoroughly after each addition with clean platinum rod; reserve filtrate; remove paper with clean platinum-tipped forceps and transfer to same platinum crucible; inspect forceps and glass siphon tube for particles of silica (if they are present, wipe with a small piece of wet filter paper and transfer to crucible).

(7) Add 1 drop of H_2SO_4 (1:1); heat carefully by indirect means until paper chars; heating is accomplished by suspending crucible inside larger platinum crucible, which is heated by Bunsen flame; place crucible plus impure silica in electric furnace and heat for 1 hour at 950°C.; transfer crucible to cooling block and desiccate over concentrated H_2SO_4; let cool for 10 minutes and transfer to balance; weigh immediately; repeat heating for $^1/_2$-hour period, weighing until two consecutive weighings check within 0.02 mg.

(8) Moisten weighed silica with water; add 1 drop of H_2SO_4 (1:1) and 1 ml. of HF; evaporate dry by indirect heating; heat at 950°C. for 15 minutes; place in cooling block and transfer to desiccator; let cool for 10 minutes and weigh immediately. The difference in weights represents the silica from first dehydration.

(9) Evaporate reserved filtrate (6) to dryness on steam bath and heat for 1 hour at 105°C.; cool, drench with 0.25 ml. of HCl (concentrated) and 2.5 ml. of hot water; digest on steam bath until salts are in solution; filter, using microfiltering apparatus; wash, using three 0.25-ml. portions of HCl (2:98) and two 0.25-ml. portions of water; transfer paper to crucible by means of platinum-tipped forceps; add 1 drop of H_2SO_4 (1:1).

(10) Heat carefully by indirect means until paper chars; place crucible plus impure silica in electric furnace and heat for 15 minutes; transfer to cooling block, let cool for 5 minutes, then transfer to balance; after 5 minutes, weigh.

(11) Add 1 drop of H_2SO_4 (1:1) and 0.15 ml. of HF; evaporate to dryness by indirect heating; heat for 15 minutes at 950°C.; transfer to cooling block; let cool for 5 minutes and transfer to balance; after 5 minutes, weigh. The difference in weight represents the silica from second dehydration.

$$\frac{\text{Combined wt.} \times 100}{\text{Sample wt.}} = SiO_2\ (\%)$$

IV. Semimicro-Determination of Alumina

(1) Weigh a 10-mg. sample in a tared platinum crucible to the nearest 0.01 mg.; add 0.1 ml. of H_2SO_4 (1:1) and 0.15 ml. of HF; heat by indirect means to fumes of SO_3; cool, rinse sides of crucible with 0.5 ml. of water; heat again to fumes of SO_3.

(2) Cool and add 2 ml. of water; digest on steam bath for 45 minutes (volume should be approximately 0.5 ml.); transfer by means of porcelain filter stick to tared microfilter beaker; wash with three 0.25-ml. portions of water.

(3) Heat on steam bath to approximately 70°C.; add slight excess of 5% 8-hydroxyquinoline (1 ml. equivalent to 4 mg. of Al_2O_3); add 2 *N* ammonium acetate drop by drop until precipitate starts to form; digest on steam bath for 1 minute; add 1 ml. of 2 *N* ammonium acetate; digest on steam bath for 15 minutes; filter, using microfiltering apparatus, and wash with five 0.5-ml. portions of cold water; wipe with damp chamois, and remove excess moisture with dry chamois.

(4) Connect microfilter beaker to vacuum and dry at 135°C. in microheater for 10 minutes; cool 2 minutes, wipe with damp chamois, and then with dry chamois; cover, and allow to stand by balance case for 10 minutes; transfer to balance, and allow to stand in balance case for 5 minutes; place on balance pan and weigh.

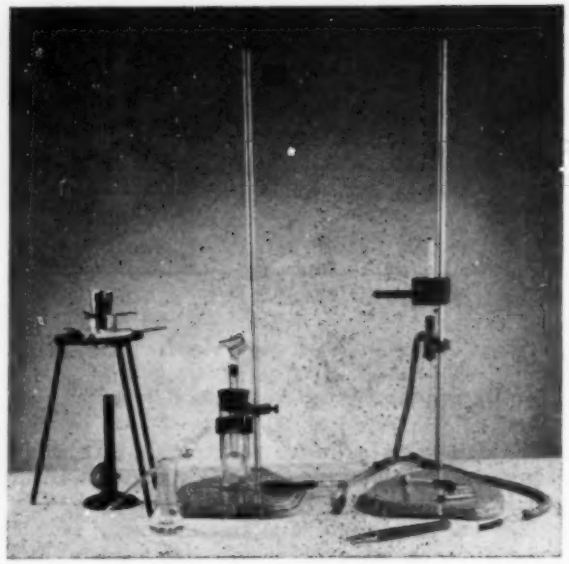


FIG. 3.—Apparatus used in semimicro-determinations.

$$\text{(5)}\quad \text{Quinolate wt.} \times 0.111 \times \frac{100}{\text{sample wt.}} = \text{apparent } R_2O_3\ (\%)$$

If iron and titanium should be present in the sample, calculation (5) will be slightly in error because of the difference in conversion factors for iron and titanium quinolates. If, however, amounts of iron and titanium are known, the true value for "R_2O_3" can be calculated as follows:

$$\text{Apparent } R_2O_3\ (\%) \text{ from paragraph (5)} + (Fe_2O_3\ (\%) \times 0.32) + (TiO_2\ (\%) \times 0.13) = R_2O_3\ (\%).$$

When amounts are large or values unknown, separate determinations of iron and titanium should be made and the corrections applied.

The foregoing procedures are nearly the same as the conventional methods except that the samples have been reduced to $^1/_{20}$ the normal size in the case of silica, and $^1/_{100}$ in the case of alumina. These changes necessitate the use of the semimicro-balance and substitution of filter sticks, microfilter beakers, and drying oven for the usual analytical tools. Another difference is that precipitates are not transferred from one dish to another, but the supernatant liquids are drawn off through the filter stick; after this is done, the precipitate and container are weighed. This procedure is intended to avoid transference losses. All of these changes make it possible to obtain results that are comparable in accuracy to macrodeterminations. Figure 3 shows some of the apparatus used in semimicro-determinations. Figures 4 and 5 are schematic diagrams of the apparatus as set up for the various steps in the procedures.

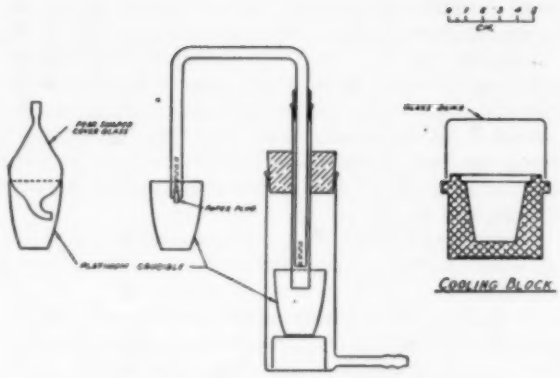


FIG. 4.—Silica filtration assembly.

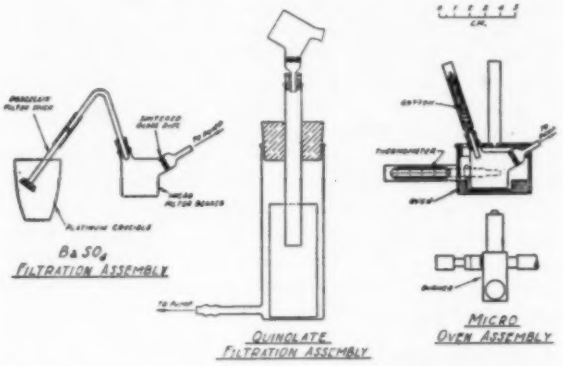


FIG. 5.—Apparatus for $BaSO_4$ and quinolate filtration and micro-oven assembly.

V. Results

Table I shows the comparative results obtained by macro- and semimicro-methods, using 8-hydroxyquinoline as a precipitant. The samples in this case were taken from a solution of aluminum chloride. The macrosample consisted of a 50-cc. aliquot, and the semimicro-sample was 0.5 cc., containing $^1/_{100}$ the amount of aluminum in the macrosamples. The two methods agree within the limits of experimental error. It may therefore be concluded that the technique and equipment employed in the semimicro-method are adequate to handle samples which amount to only $^1/_{100}$ of the ordinary analytical sample.

Table II gives the results obtained for aluminum oxide on samples of National Bureau of Standards glasses. In this case also, the samples used in the semimicro-method have been cut to $^1/_{100}$ of the usual amount but the results are within the usual experimental error. Figures shown for aluminum oxide have been corrected for the iron and titanium oxides present that were coprecipitated with the 8-hydroxyquinoline.

In Table III are shown the results of silica determinations made on National Bureau of Standards glasses. The results obtained by the semimicro-method are in satisfactory agreement with the full-scale determinations.

Table IV shows a number of analytical results obtained on various types of inclusions. The first column under each heading gives the analysis of the clear glass surrounding the inclusion; the second column under each heading gives the results obtained on the lump or stone. As indicated by asterisks, some of these results were obtained by ordinary macromethods and others by means of the semimicro-procedures described previously.

TABLE I

ALUMINA DETERMINATION BY MACRO- AND SEMIMICRO-METHODS*

8-hydroxyquinoline precipitation (Al_2O_3 mg./ml.)	
Macromethod	Semimicro-method
2.012	2.04
2.013	2.04
	2.05

* All samples, aliquot portions of same $AlCl_3$ solution.

TABLE II

ALUMINA DETERMINATION IN NATIONAL BUREAU OF STANDARDS GLASSES

Glass No.	Al_2O_3 present (%) (certificate value)	Al_2O_3 found (%)	
		Macromethod (1-gm. sample)	Semimicro-method (10-mgm. sample)
80	0.33	0.29	0.28
		0.29	
93	1.92	1.91	1.89
		1.92	
128	1.89	1.88	1.83
		1.88	1.85

TABLE III

SEMIMICRO-DETERMINATION OF SILICA IN NATIONAL BUREAU OF STANDARDS GLASSESS

Glass No.	SiO_2 present (%) (certificate value)	SiO_2 found (%) semimicro-method (50-mg. sample)
80	74.1	73.9
93	80.1	80.1
128	69.5	69.4

TABLE IV

TYPICAL ANALYSES OF CORDS AND STONES

Sample No.	Description	SiO_2 (%)		R_2O_3 (%)	
		Matrix	Inclusions	Matrix	Inclusions
1	Rough glass	67.46	67.05	2.97	3.41
2	Lump, center opaque	74.24	75.90	5.56	6.25
2a	Opaque center, sample No. 2	74.24	66.84	5.56	24.46
3	Clear lump	67.63	66.20	2.84	6.77
4	Clear lump	75.38	78.14	5.27	4.79
5	Stones	67.66	58.13*	2.87*	15.36*
6	Clear lumps	66.90	66.21*	2.85	6.96*
7	4 lumps, centers opaque	74.50	76.44*	5.26	5.54*
8	Egg-shaped lump	74.99	75.66*	5.73	5.95*
9	5 round lumps, centers light brown	74.99	73.33*	5.73	6.85*
10	Clear colorless cord	74.51	74.25*	5.78	5.93*
11	Colorless lumps, centers white opaque	74.52	75.74*	5.42	5.56*

* Microanalysis.

In sample No. 1, because no crystalline center was observed, no petrographic examination could be made, and chemical analysis was the only means of identification. The lumps show an increase in R_2O_3 content at the expense of silica.

Sample No. 2 was a large stone with an opaque white center. The lump as a whole shows a high content of silica and R_2O_3, whereas the central crystalline portion (sample 2a), by chemical analysis, shows only high alumina. Petrographic examination showed the crystalline phase to be mainly cristobalite. This is a case in which a chemical analysis supplements the petrographic findings because the petrographic examination suggested only the presence of siliceous material.

The lump in sample No. 3 shows a preponderance of R_2O_3 over silica as compared with the base glass, indicating contamination of the glass by some type of aluminous refractory.

Sample No. 4 consisted of a stone which was found by petrographic examination to contain tridymite; the chemical analysis also shows an excess of silica.

The crystalline material in sample No. 5 was identified as nephelite with a corundum center; chemical analysis shows also high alumina in the stone as a whole.

In sample No. 6, all lumps investigated by chemical and petrographic analyses were of the same general appearance; the chemical analysis of one clear lump, however, showed a high percentage of alumina whereas the petrographic analysis indicated an excess of silica. Subsequent work indicated that the lumps were produced by the action of alkali silicates running over aluminous flux block and thence into the glass.

Sample No. 7 was also a case in which the content of silica and alumina were higher in the lumps than in the clear glass as shown by chemical analysis; petrographic tests showed only nephelite. The excess of silica could therefore have been found only by use of the microprocedure, because these samples were very small.

Samples Nos. 8, 9, and 10 are examples of inhomogeneities in various glasses which showed no crystalline material; no petrographic examination, therefore, was possible. In each case, after isolating the lump or cord, the sample was so small that the semimicromethod furnished the only source of information as to the origin of the inclusions.

The stone in sample No. 11 showed an excess of 1% of silica, and the crystalline phase was found to be cristobalite.

In each of the examples cited, chemical analysis served to reveal significant differences in composition between the inclusion and the surrounding glass. Where the inclusion is small (less than 0.25 gm.), ordinary methods of chemical analysis do not apply, and microprocedures must be used. In the case of a vitreous lump, chemical examination is the only practical method of obtaining information as to the probable origin of the inclusion. Even when crystalline material is present, the chemical examination furnishes a valuable supplement to petrographic findings.

It was not the purpose of this paper to discuss the results obtained from the standpoint of furnace operations. The results of such chemical analyses, however, can be of great assistance in locating difficulties in furnace operation when they are coupled with careful observation on the furnace itself and familiarity with current operating conditions.

Acknowledgment

The writers wish to express their thanks to Herbert K. Alber and A. A. Benedetti-Pichler for suggestions in selecting equipment and working out procedures.

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SURFACE TENSION AND PERSISTENCE OF CORDS IN GLASS*

By Mellen A. Knight

Abstract

The action of surface tension in molten glasses is discussed in relation to cord persistence. An examination is made of the reported mechanism for the solution of cords as proposed by Jebsen-Marwedel. His viewpoint that the shape of immersed cords is governed by surface-tension differences between the cord and matrix glasses appears to be in conflict with the physics involved. The possible influences of interfacial tension on the shape of cords and on their location *in* or *on* the melt are considered along with its relation to other physical forces. It is concluded that the only stable form for cords under the influence of interfacial tensions alone is a spherical one. Other factors, such as high viscosities, varying diffusion rates, and mechanical and thermal stirring cause the irregular shapes found in practice. The relation of surface tensions to these factors requires further study.

I. Introduction

On the problem of the homogenizing of cordy glass, the influence of the relation between the individual surface tensions of the matrix and cord glasses has been discussed by several writers.[1] In these articles and in discussions at recent technical meetings, considerable emphasis has been laid on these surface tensions as the predominant factors in regulating cord persistence. An examination of this problem in the light of the basic physics involved raises doubt as to the accuracy of the picture that has been presented regarding the effects of the surface-tension forces on the shape of the cords. The present note is not concerned with the correctness of the experimental data relating to the influence of chemical composition either on surface tension or cord persistence but deals only with the manner in which surface-tension differences regulate the shape and rate of solution of cords.

II. Literature

A frequent statement in the literature is that a cord glass having a surface tension lower than that of the matrix glass will dissolve readily in the matrix, whereas a cord of surface tension higher than that of the matrix will dissolve but slowly. The reported experimental evidence has supported this conclusion. In discussions of this phenomenon, however, little or no attention has been paid to the pertinent differences between floating and immersed cords. The explanation offered by Jebsen-Marwedel[1(a)] for the effect has been cited in the literature.

In discussing completely immersed cords, Jebsen-Marwedel stated that if the glass comprising the cord has a higher surface tension than the matrix glass the cord will draw up into a circular cylinder, thereby presenting little surface and dissolving very slowly. On the other hand, if the cord has a lower surface tension than the matrix glass, the cord is assumed to take on a starlike cross section, with the large surface causing ready solution in the matrix glass. He based these conclusions on a series of contact experiments between pairs of molten glasses of various surface tensions. These experiments illustrate clearly the well-known conditions for the spreading of a liquid with a lower surface tension on the surface of one with a higher surface tension. It is not apparent, however, that the results can be applied to the case of totally immersed cords. Not only is the starlike shape which is attributed to the lower surface-tension cords not found in ordinary low-temperature and low-viscosity liquid mixtures, but it also appears to have no sound physical basis.

III. Cords and Surface Tension

If a particle of fluid is left free from extraneous force, it will form a sphere under the influence of surface tension. Actually the "surface tension" is the interfacial tension between liquid and air, or, in some cases, between oil or some other fluid, the globule being completely immersed in the air or oil as the case may be. According to Jebsen-Marwedel's hypothesis, the assumption is made that if the globule were immersed in a liquid having greater surface tension than itself, the sphere would collapse to a hollow-cheeked tetrahedron, exposing a maximum of surface to the matrix fluid and inviting solution in that fluid, but this is not the case. If, instead of a globule of water or of molten glass in air, a globule of air is present in water or in molten glass, the shape is still a spherical one; similarly, whether oil is dispersed in water or water in oil, as long as the dispersed phase (globule) is completely immersed, its form is spherical. Apart from the ex-

* Presented at the Forty-Sixth Annual Meeting, The American Ceramic Society, Pittsburgh, Pa., April 4, 1944 (Glass Division). Received December 30, 1943.

[1] (*a*) H. Jebsen-Marwedel, "Influence of Surface Tension of Slag Glasses from Refractory Materials on Their Tendencies to Form Cords and Streaks," *Glastech. Ber.*, **15** [5] 163–73 (1937); *Ceram. Abs.*, **17** [5] 177 (1938); "Remarks on Influence of Surface Tension in Glassmelting Processes," *Jour. Soc. Glass Tech.*, **21** [88] 436–41 (1937); *Ceram. Abs.*, **17** [9] 304 (1938).

(*b*) A. E. Badger and H. R. Pinnow, "Vanadium and Chromium Oxides in Refractories as Aids in Elimination of Cords in Glass," *Glass Ind.*, **22** [4] 161–62 (1941); *Ceram. Abs.*, **20** [7] 168 (1941).

(*c*) W. B. Silverman, "Surface Tension of Glass and Its Effect on Cords," *Jour. Amer. Ceram. Soc.*, **25** [6] 168–73 (1942).

(*d*) A. E. Badger, C. J. Uhrmann, and A. C. Ottoson, "Use of Lead Oxide in Glassmaking Refractories," *Glass Ind.*, **24** [11] 465–67, 478, 486 (1943).

perimental evidence of everyday experience which shows that these globules are always spherical (insofar as surface tension or interfacial tension can control them), it is quite evident that with a hollow tetrahedron or some other irregular figure, the radius of curvature of the surface would vary from place to place and would therefore require different internal pressures to balance it. In particular at the very sharp corners of the tetrahedron, an infinite pressure would be needed inside the bubble or globule, whereas at the hollow sides of the tetrahedron, a reduced pressure would be necessary. By definition, however, the globule is a fluid and can have only one and the same pressure in all places. This pressure arises from the attractions and repulsions of its own molecules and is therefore inherently the same at all points.

In the case of the two-dimensional, rather than the three-dimensional problem, an elongated circular cylinder is found instead of a sphere and the same principles apply. There is nothing about surface tension that can collapse a circular cylinder of cord to a "hollow-ground" triangular razor or bayonet. The shape will remain a circular cylinder, whether or not the surface tension of the matrix or the cord is greater, as long as the surface tension can control it. The nonspherical shapes found in many cords, drawn out into ribbons or "ream," are caused by the resistance of viscosity to the efforts of the interfacial tension to produce the spherical shape. The comparative stability of these cords, which are very elongated cylinders, depends on the high viscosities of the two phases that have the effect of anchoring the ends of the cord, as it were, at a distance apart. If this virtual anchoring did not take place, the cord would contract until it formed globules. As far as interfacial tensions are concerned, the only form of an immersed cord that is completely stable is a sphere.

All cords are therefore to some extent unstable, but since a typical cord may be hundreds of feet long and only a few wave lengths in diameter, the inability of the cord to contract endwise to a globule is obviously a very different matter quantitatively from its ability to form a circular shape in cross section. It is true that many cords are not circular in cross section but rather are flat and ribbon-like; this fact also is due to the stirring of the liquid and to its high viscosity. The surface tension of itself certainly will not draw out a globule into an elongated cylinder, and it is equally certain that surface tension will not of itself collapse an elongated circular cylinder into a triangular or hollow-sided one. Insofar as surface tension has any say in the matter, the cylinder will always be brought to a circular shape in cross section, and this will be true whether the cord or the matrix has the higher surface tension when measured against air.

In the case of these immersed cords, the only surface energy present (in the vicinity of the cord) is the interfacial tension between the cord and matrix glasses. Since almost all commercial glasses are completely miscible with each other in the molten state, any apparent immiscibility is merely a kinetic matter of viscosities, diffusion rates, and mixing, representing a nonequilibrium condition. In mixtures of the molten glasses, the interfacial tensions would be expected to be zero or negative, as in all pairs of miscible liquids. (The term "negative" is used here in the usual manner to indicate that the net attractive forces on the surface molecules of a liquid are directed away from the body of that liquid.) Since the glass-air surface tensions and glass-glass interfacial tensions are all functions of the interionic forces in the glasses, these tensions are related; and in various pairs of glasses, each of similar compositions, these relations can be expected to be somewhat analogous. Interfacial tensions, nevertheless, cannot be calculated from the individual surface tensions of the component glasses. Further complications arise through the diffuse nature of the boundary between two glasses, which may considerably modify the forces involved. The variation of diffusion rates with chemical composition causes certain cords to be more persistent in glass than other cords. Differential diffusion leads also to marked changes in the composition of the cord during solution. It appears that diffusion phenomena are very important in cord persistence, both in immersed cords and in floating cords.

The behavior of heterogeneities or differences of composition on the surface of molten glass, that is, at the flux line in the tank or pot, is another matter altogether. Three phases are present here, namely, the matrix, the cord, and the furnace atmosphere, and each pair of these phases has its particular interfacial tension. The relationship between these tensions regulates the contribution of surface-tension forces to the spreading or nonspreading of the contamination on the surface of the glass. The usual conditions apply for the spreading of a liquid on the surface of a second liquid of higher surface tension than the first. Since these are discussed in treatises on surface tension, they need not be considered further here. The complete role of surface tension in surface cords, however, is by no means clear. Factors, such as viscosities and stirring, affect the spreading of cords. Surface tension is only one of several forces that contribute to the sinking of cords which are floating or only partially immersed; density differences, mechanical and thermal stirring, and viscosity also must be considered. The relation of surface tension to these other factors needs further study.

IV. Summary

Interfacial tension is only one of several factors which influence the spreading and the sinking of surface cords. Changes in chemical compositions of glasses obviously cause variations in all of their physical properties. This must be considered when the relation of surface tensions to any experimental effect is being studied. It appears that in immersed cords there is no sound physical basis for attributing any shape other than that of a sphere to the influence of interfacial tension alone. Lengthening and flattening in immersed cords is caused by the thermal and mechanical mixing of the viscous liquids and not by any surface-tension relationships. Diffusion rates (which are obviously related to the same ionic forces that govern viscosities

and interfacial tensions) are a measure of the net rate of solution of cord glass, whether the cord is immersed or floating. The importance of surface tension in the persistence of cords in glass, however, should not be overemphasized. Further studies may show that various other physical properties of molten glasses have greater influences than has surface tension.

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SURFACE LAYER OF SHEET GLASS*

BY F. L. BISHOP, JR.

ABSTRACT

This research was conducted to obtain evidence of the nature of the fire polish on sheet glass. Three measurements were made on each sample as follows: (1) The deviations from Fresnel's reflection laws, (2) a measurement based on the Pfund method of determining the apparent Brewsterian angle as compared to that calculated from the index of refraction of the glass, and (3) the true index of refraction by a prism method in which the samples were cut and ground to 60-degree prisms. These measurements showed that freshly drawn sheet glass probably has a crystalline layer several molecules thick on the surface. The layer has a high index of refraction, but this is counteracted quickly by water absorption if the glass is dampened slightly or is exposed to the atmosphere.

I. Introduction

This research study of fire polish on sheet glass is based on Brewster's law, which states that the tangent of the polarizing angle is equal to the index of refraction of the medium on which the light is incident, and on the group of Fresnel equations giving the reflecting power of a dielectric.[1] Early tests confirmed the Fresnel equations rather completely, but in 1886 Lord Rayleigh[2] found deviations of nearly 7% from theoretical values when he investigated polished surfaces of black glass. Maclaurin[3] and Drude[4] set forth theoretical equations to explain these deviations on the basis of a surface layer with a different index of refraction from that of the base glass.

II. Research Procedure

Plane-polarized light with its plane of polarization 45 degrees from the plane of incidence was reflected at Brewster's angle from the glass in question. According to Fresnel's equations, this light should be reflected as plane-polarized light with its plane of polarization

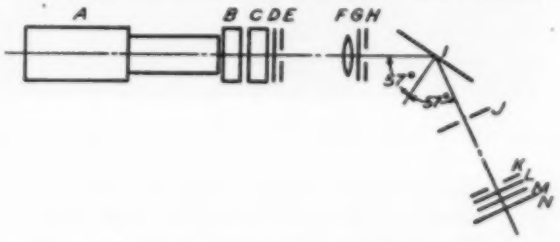

FIG. 1.—Diagram of setup; *A*, Balopticon projector; *B*, copper chloride solution; *C*, potassium bichromate solution; *D*, Wratten No. 44 filter and ground glass; *E*, aperture, 15 by 15 mm.; *F*, collimator lens; *G*, H-type Polaroid; *H*, adjustable diaphragm and shutter; *I*, test sample; *J* and *K*, 20-mm. circular apertures; *L*, quarter-wave plate; *M*, H-type Polaroid split into two fields with polarizing axes 5 degrees apart; and *N*, film in Argus-type A camera with lens removed.

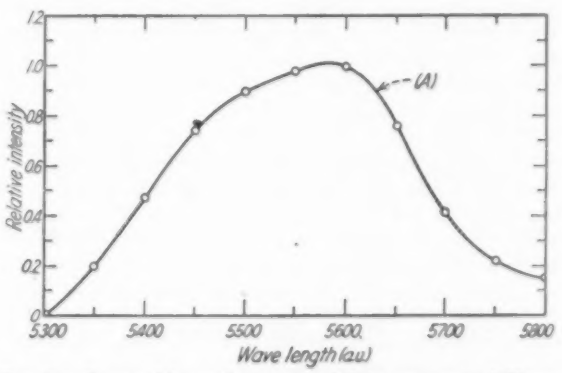

FIG. 2.—Spectral intensity curve of light source and filters used.

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Based on a thesis submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy, University of Pittsburgh, June, 1942. The research was conducted in the Jeannette plant of the American Window Glass Company in cooperation with the University of Pittsburgh.

[1] For a discussion of the Fresnel equations and their application to light incident on glass, refer to the text by Frances A. Jenkins and Harvey E. White, Fundamentals of Physical Optics, pp. 388–98. McGraw-Hill Book Co., New York, 1937.

[2] (*a*) Lord Rayleigh, *Phil. Mag.*, **232**, 444 (1908).

(*b*) Lord Rayleigh, Collected Papers, Vol. 3, pp. 496 and 523. Published in 1899.

[3] R. C. Maclaurin, "Intensity of Light Reflected from Transparent Substances," *Proc. Roy. Soc.* [London], **79**, 18 (1907).

[4] P. L. Drude, Theory of Optics (tr. by Mann and Millikan), pp. 278–95. Longmans, Green & Co., 1902.

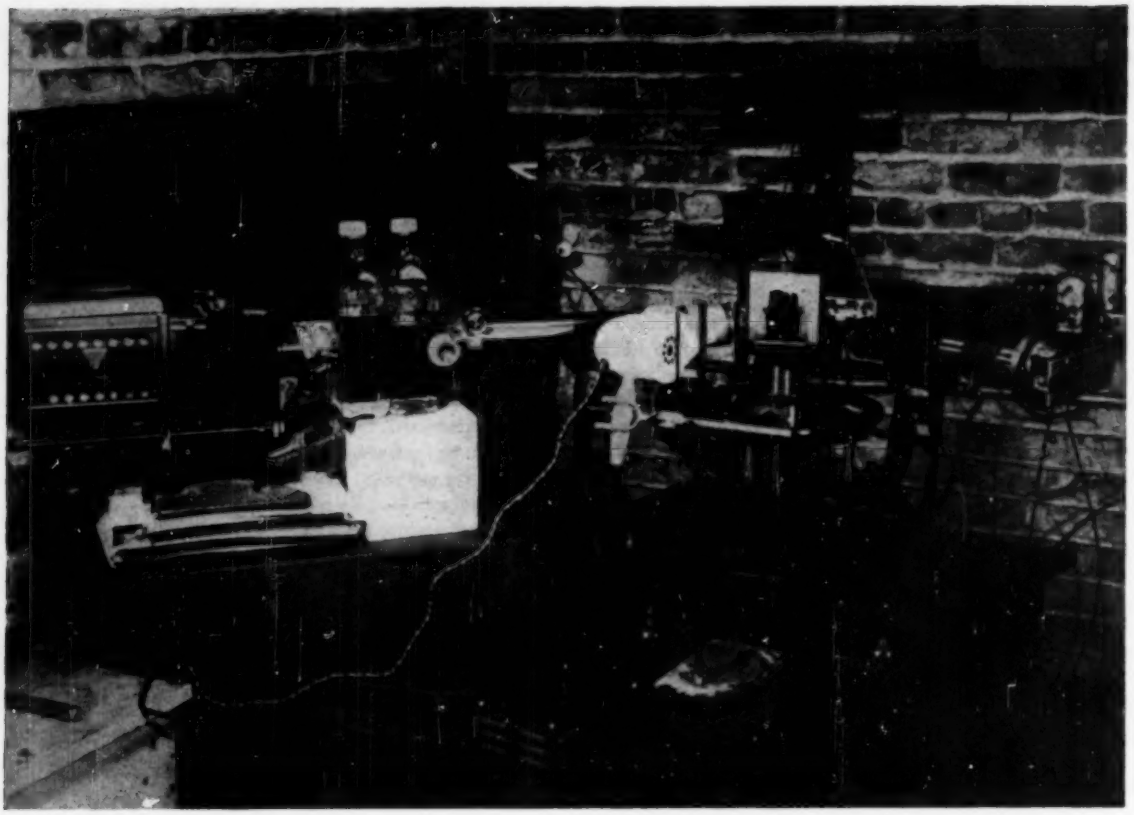

FIG. 3.—Photographic setup.

parallel to the glass surface. Because of a surface layer, however, the light showed a slight elliptical polarization. This ellipticity was measured with a quarter-wave plate analyzer (see Fig. 1).

A 500-watt tungsten projector lamp was used as a light source. The light was focused on a piece of ground glass by a Bausch and Lomb Baloptican projector. In the light path were two filter cells, each approximately 40 mm. in depth. The first of these cells contained a saturated solution of potassium dichromate in water, and the second cell, a saturated solution of cupric chloride. The effect of these solutions was to give a rather narrow band of transmitted light which had a maximum in the green at about 5600 a.u. (see Fig. 2). An opening approximately 15 mm. square replaced the slit of a large spectroscope with 60-mm. lenses. The ground glass in this opening acted as a secondary source of light, and the usual lens was focused at the exit end of collimator to give parallel light. A permanently mounted polarizing plate of the H-type Polaroid was also on the exit end, with the polarizing axis at 45 degrees to the vertical. A camera shutter and diaphragm were mounted over this polarizer, and the diaphragm was set to give a 10-mm. diameter beam. The shutter was used only in preliminary work to keep the Polaroid clean between test runs. The sample to be tested was mounted in a universal mounting on the spectroscope table.

On the entrance end of the analyzer tube was mounted a limiting diaphragm, 20 mm. in diameter, used to eliminate extraneous light. On the exit end were mounted, in order, a quarter-wave plate in a revolvable mount with a circle and vernier for reading minutes of arc, a split-field analyzer of the H-type Polaroid, and a camera back from an Argus-type A camera to carry 35-mm. film.

The split-field analyzer was made by cutting a 40-mm. circle of Polaroid across the diameter at an angle of about $2^1/_2$ degrees with the polarizing axis and remounting it with one piece turned over so that the axes were 5 degrees apart. This arrangement yielded the best results because it balanced the two factors, namely, insufficient light transmission at low angles and great difficulty in getting a short exposure scale with greater angles (see discussion by Adams and Williamson[5]). The light passing through the analyzer fell on the film which, except for the condition of perfect balance (or at 90 degrees to it), showed two half circles with a degree of blackening proportional to the transmission of the Polaroid half circles at the angle being measured. The film was developed in Defender 777 to 1.3 gamma.

The length of exposure was set on a Fink Roslieve

[5] L. H. Adams and E. D. Williamson, "Annealing of Glass," *Jour. Franklin Inst.*, **190**, 216, 597–631, and 835–70 (1920).

electronic timer, which controlled the projector lamp. To make a determination of a balance point, a series of identical exposures was made, changing the setting of the analyzer or of the quarter-wave plate by 10- or 5-minute steps from a point 2 degrees on one side of the visually determined balance to 2 degrees on the other side. This procedure yielded considerable difference in the blackening of the film at the extreme positions, ranging down to very small differences near the point of balance.

The degree of blackening of each sector of each exposure was measured on a photometer, which consisted of another Baloptican projector with a $^1/_4$- by $^1/_8$-in. slit opening, focused through the film on a Weston photronic cell; this cell in turn operated a research Sobel-type galvanometer. Across the galvanometer was a variable resistance box to act as a shunt control (see Fig. 3).

III. Data and Equations

When the blackening was evaluated, the differences for each change of analyzer or quarter-wave plate angle were worked out and plotted against angle on cross-section paper. The balance point is that point where the difference plot crosses the zero axis (see Fig. 4).

The values so obtained were used in Drude's[4] equations to give values of surface-layer thickness. Two other values were necessary to complete these equations. One of these, an accurate determination of the index of refraction of the base glass, was obtained by cutting all samples in the form of a triangular prism and, after polishing their new surfaces, measuring the angle of minimum deviation. This measurement was made visually with another spectroscope.

The other determination was not so accurate. It was made by the Pfund method,[6] which depends on the measurement of the apparent Brewsterian angle as compared with that calculated from the measurement of the angle of minimum deviation.

IV. Glasses Tested

Because the primary purpose of the investigation was to determine the properties of that surface of glass generally referred to as "fire polished," great care was taken in obtaining samples of freshly drawn sheet glass. Samples were cut while the glass was still hot from the drawing operation. No oil or other lubricant was used on the cutting wheel. The glass was placed immediately in a hermetically sealed box which was kept at 30°C. until ready for test to prevent condensation of moisture on the glass. During the actual test for Fresnel deviations, a current of hot air was blown on the glass at approximately the same temperature. The glass was kept under conditions similar to those for the Pfund-method tests, but no other particular precautions were taken. The surface conditions had practically no influence on the minimum-deviation

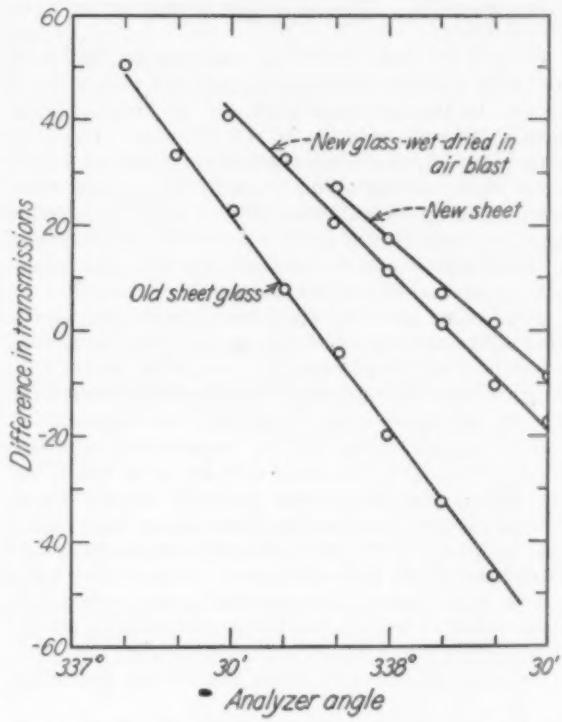

FIG. 4.—Difference in light transmissions through two half fields plotted against analyzer angles.

method for measuring the index of refraction of the body of the glass.

For samples other than those noted as fresh glass, similar precautions were taken as far as possible.

To test the accuracy and reproducibility of the measurements made on the deviations from the Fresnel values, a series of tests was made using five samples cut from a single sheet of stock sheet glass. Five measurements were made on each sample. The twenty-five readings gave an average of $+27.9 \pm 0.6$ minutes of arc from the vertical position of the analyzer. This result corresponds to a coefficient of ellipticity (ρ in Drude's calculations[4]) of $+0.0080 \pm 0.0002$. On all other types of glass tested, at least three samples were taken and two runs were made on each sample. Except in the case noted, no measurement varied more than two minutes of arc from the averages reported.

The most important samples tested were those of fresh sheet glass which had been kept dry and warm until tested. Twelve samples of this glass taken over a 14-day period gave a Fresnel deviation of -7 minutes of arc corresponding to $\rho = -0.002$. The index of refraction of the glass by minumum deviation and by Pfund's method was 1.513. Because the value of ρ is negative, the surface layer must have a higher index than the glass and no minimum thickness of surface layer can be calculated according to equation (52) of Drude. By assuming the surface to be crystalline quartz, however, the layer can be calculated according

[6] A. H. Pfund, "Brewsterian Angle and Refractive Indices," *Jour. Optical Soc. Amer.*, **31**, 679–82 (1941); *Ceram. Abs.*, **21** [3] 64 (1942).

to equation (48). This calculation gives a surface layer 39 a.u. thick.

Four of the test samples of newly made glass were wet with a spray of distilled water and then allowed to dry in the warm-air blast for 24 hours. These gave a Fresnel deviation of +2 minutes. The base glass index of refraction as well as the apparent Pfund value were, of course, unchanged. There was, however, a change of 9 minutes of arc caused by a water layer retained on the glass or by some solubility and chemical activity on the surface. To give this change of 9 minutes requires a water layer 15 a.u. thick.

Four other samples of the new glass were given a very light polishing with black rouge. They were then washed in distilled water and dried in an air blast. This treatment had the opposite effect because it lowered the Fresnel deviation to −18 minutes, an ellipticity of −0.005, and a change of −11 minutes from the new glass value. The base glass had the same index, but the Pfund method yielded a slightly higher value, namely, 1.519. Because the nature of the layer in this case is unknown, the only value of layer thickness obtained was from the substitution of the Pfund value as the layer index. This method gives an extremely large value of 585 a.u. and casts great doubt on the value of the Pfund method of measurement.

The samples of stock sheet glass listed previously with a deviation of 27.9 ± 0.6 minutes had an index of refraction by the minimum-deviation method of 1.514 and Pfund values varying from 1.485 to 1.490. These figures give a layer thickness of 236 a.u. by equation (48) of Drude when the Pfund value is used and, by equation (52), a value of minimum thickness of 39 a.u.

V. Summary

Newly drawn sheet glass probably has a crystalline layer several molecules thick as a result of fire polishing. This layer is of higher index of refraction than the glass, but it is counteracted by the rapid absorption or chemical action of water as soon as the glass is dampened even for a very short time. This water or water-soluble layer explains the high transmission of sheet glass. Because the index of refraction of the layer is not known, the effect cannot be calculated accurately. It is possible that the alkali atoms are replaced in the surface layer either by absorption from the air or by migration through the glass from beneath. Plate glass and polished sheet glass show a layer of higher index of refraction, probably as a result of the iron compounds used in polishing.

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RAPID METHOD FOR ESTIMATING SODA IN GLASSES, II*

By S. R. Scholes and Eric de R. Falcão

In the titration method for estimating soda in glasses previously described,[1] an improvement has been made by using only an aliquot portion of the final filtrate, thus eliminating washing.

For convenience, the steps of the method are reviewed: The 60-mesh sample (1.000 gm.) is evaporated with H_2F_2 and H_2SO_4 and heated to dense fumes. The residue is taken up in water and treated with milk of lime to phenolphthalein alkalinity; the solution is then boiled and filtered. The precipitate of hydroxides and calcium sulfate is washed white. Barium hydroxide, 2.5 gm., is dissolved in the filtrate to convert sulfates to hydroxides. Carbon dioxide is passed into the solution until the pink color disappears, and the boiling removes excess CO_2 and restores the color.

The solution is transferred to a 250-ml. flask, cooled, and made up to the mark. After mixing, the solution is filtered (starting with dry paper and funnel) into a 200-ml. flask to the mark. This 200-ml. volume is transferred to a suitable beaker and titrated with standard acid to an end point with bromophenol blue or similar indicator. The calculated value for grams of Na_2O, multiplied by 1.25, gives the amount of Na_2O in sample.

The true volume of solution of $NaHCO_3$ and Na_2CO_3 before filtering is, of course, less than 250 ml. by the volume of precipitated barium salts present. The latter, however, can be shown to be less than 0.4 ml., and the correction would be a subtraction of 0.0016 of the percentage of Na_2O found, a difference within the usual error in alkali determinations.

* Received March 20, 1944.

[1] S. R. Scholes, "Rapid Method for Estimation of Soda in Glasses," *Jour. Amer. Ceram. Soc.*, **16** [7] 342–43 (1933).

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FUNDAMENTAL STUDY OF CLAY: VI, FLOW PROPERTIES OF KAOLINITE-WATER SUSPENSIONS*

By F. H. Norton, A. L. Johnson, and W. G. Lawrence

Abstract

The flow properties of six monodisperse kaolinite fractions were studied over a large range of concentration. From these results, it has been possible to set up an equation relating viscosity to concentration which holds over a very wide range. Equations relating concentration to thixotropy and to the yield point which have general application could also be established. The viscosity of a suspension is obtained from the sum of three quantities, namely, those contributed by (1) the liquid, (2) the individual particle, and (3) the collisions of the particles. Thixotropy is found to be due to the sum of two quantities, namely, the contribution of (1) the individual particle and (2) the interference of the particles. The yield point in these fractions was found to be proportional to the cube of the concentration. With these relations, it is possible to calculate the viscosity of a casting slip for any change in specific gravity.

I. Introduction

Before beginning a minute consideration of the suspensions, it will be helpful first to draw a picture that will fit in reasonably well with the general knowledge, even though it may be but a rough sketch, and then to add details as they are revealed in later discussions.

The dilute flowing suspension, subject to a velocity gradient and the resulting shearing strain, is composed of individual plates or groups of plates revolving about an axis in the shear plane as shown to scale in Fig. 1.

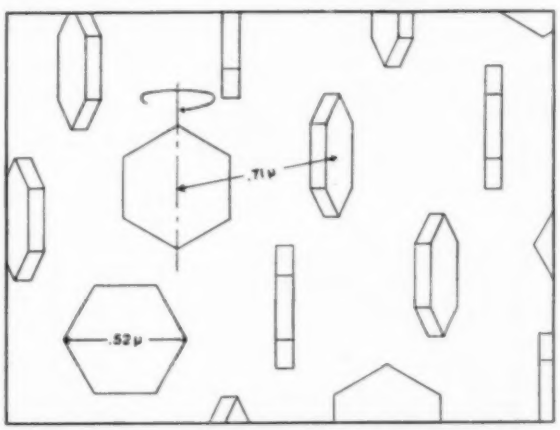

Fig. 1.—Cross section of particles of No. 5 fraction containing Na kaolinite at a viscosity of 0.017 poise and a volume concentration of 0.05 solid.

The angular velocity of a particle will be greatest when the plate is normal to the shear plane and lowest when it is parallel to it. A larger proportion of the plates will therefore be parallel to the shear plane than normal to it, which gives a preferred average orientation to the particles and thereby produces the so-called streaming effect observed when a dilute anisotropic suspension is agitated. As the suspension becomes more concentrated, the particles cannot revolve freely because of the nearness of their neighbors and a sliding action results as shown to scale in Fig. 2.

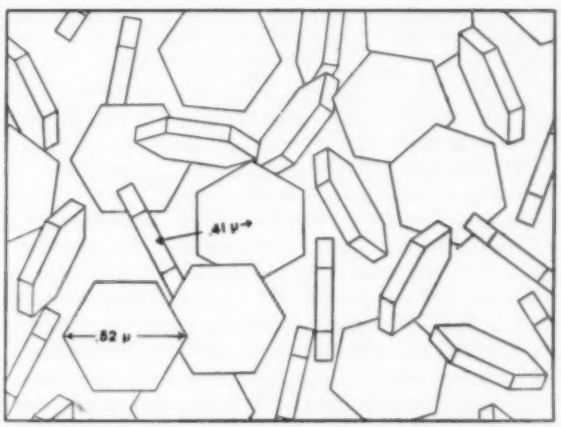

Fig. 2.—Cross section of particles of No. 5 fraction containing Na kaolinite at a viscosity of 3 poises and a volume concentration of 0.28 solid.

The particles, in addition, have an irregular motion due to the bombardment of the water molecules, a movement of consequence only in the smaller sizes. Because of this irregularity and the rotation, particles or groups are constantly colliding and breaking apart so that energy is absorbed in the form of heat (1) by the shearing of the liquid, (2) by the movement in the liquid of the individual particles or groups, and (3) by the collisions of particles with each other.

Little information is available concerning the size of the particle groups. In deflocculated suspensions, they must be quite infrequent because both microscopic and settling studies indicate that the great majority of the particles act as individuals owing to the negative charges which cause repulsion forces. Flocculated suspensions, however, contain visible large particle groups at low shear rates, but there is no way of knowing how much they are broken down at high shear rates.

When a flocculated suspension is allowed to stand

* Presented at the Forty-Sixth Annual Meeting, The American Ceramic Society, Pittsburgh, Pa., April 4, 1944 (White Wares Division). Received February 5, 1944.

quiet for a short time, a yield point can be measured in most cases. The yield point is greater in concentrated than in dilute suspensions, that is, the particles form some sort of a rigid network, either real or held together with forces acting through the water medium. Yield points have been determined in suspensions of kaolinite at a volume concentration of 0.005 solid when flocculated. With more sensitive means of measurement, however, yield points might be found at still lower dilutions.

There is nothing in the preceding picture that is not in general agreement with the research results of numerous physicists and colloidal chemists working in this field. The main purpose of this paper, therefore, is to add details based on the results obtained from some particularly pure kaolinite suspensions.

II. Flow of Suspensions in General

The units and symbols used throughout this paper will conform with those of the Society of Rheology.

F_0 = yield stress (dynes·cm.$^{-2}$).
F = shearing stress (dynes·cm.$^{-2}$).
$\frac{dv}{dr}$ = rate of shear strain (cm.·sec.$^{-1}$·cm.$^{-1}$).
η_a = coefficient of apparent viscosity of suspension (dynes·sec.·cm.$^{-2}$) ($ML^{-1}T^{-1}$) (poise).
η_1 = coefficient of viscosity of suspending medium.
η_0 = basic viscosity of suspension.
θ = coeff. of thixotropy (dynes·cm.$^{-2}$) ($ML^{-1}T^{-2}$).
C = vol. concentration of solid in relation to total volume.
YP = yield point at zero rate of shear strain.

The flow properties of suspensions, unless extremely dilute, show distinct differences from the flow in a Newtonian liquid. In the first place, the coefficient of viscosity is higher owing to the energy absorption of rotation and collision of the particles. If the shearing stress be plotted against the rate of shear strain, a straight line does not necessarily result nor does it usually pass through the origin and it is impossible to obtain a real value of viscosity. In suspensions, therefore, reference is made to the coefficient of apparent viscosity at some particular rate of shear strain which is determined by the reciprocal slope of the curve under these conditions. Most of the suspensions of interest to ceramists show an increasing slope with increased rates of shear (curve *B*, Fig. 3), and this property of decreasing coefficient of viscosity is known as thixotropy. The evaluation of thixotropy is carried out by the method suggested by Goodeve and Whitfield.[1] The apparent viscosity coefficient is plotted against the reciprocal of the shear strain rate and the curve extrapolated to $\frac{1}{dv/dr} = 0$, which in effect gives the conditions at infinite rate of shear. This is termed the basic viscosity coefficient or η_0; η_0 is, of course, greater than the η for the liquid; in kaolinite suspensions, however, it is never reached and is therefore only of academic interest. The coefficient of thixotropy is given by the slope of the tangent to this curve at the 0 axis. An example of the determination of the coefficient of thixotropy is shown in Fig. 4.

[1] C. F. Goodeve and G. W. Whitfield, "Measurement of Thixotropy in Absolute Units," *Trans. Faraday Soc.*, **34**, 151-20 (1938).

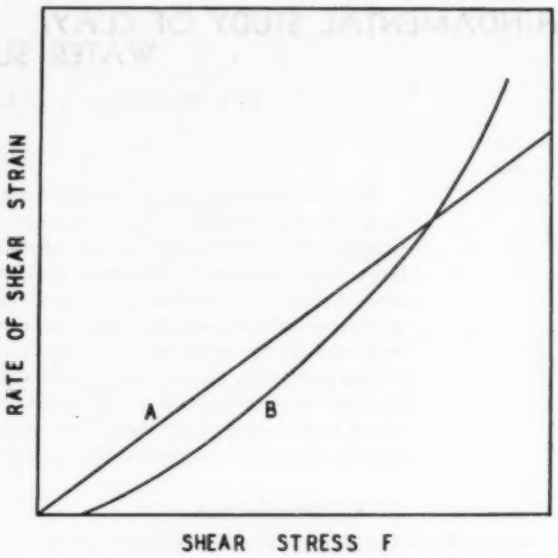

FIG. 3.—Flow properties of suspensions.

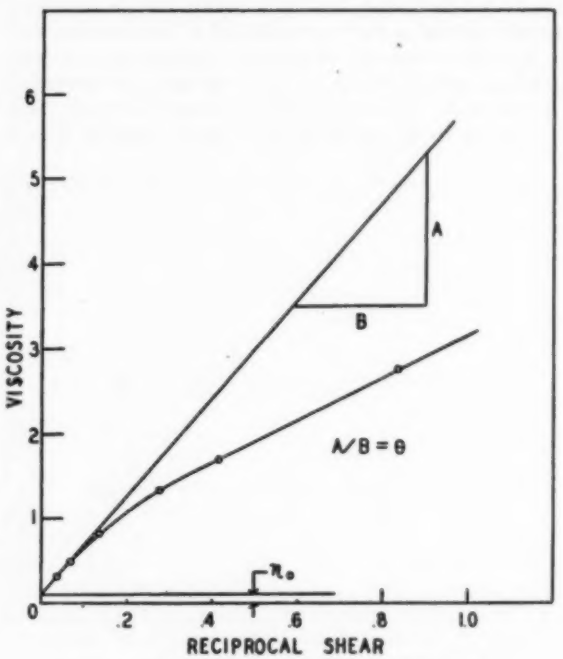

FIG. 4.—Method of determining thixotropy.

A second characteristic shown by certain types of suspension is the property of increasing apparent coefficient of viscosity with increase in shear strain rate, which is known as dilatency. It might be thought at first that this is negative thixotropy. It is actually nothing of the kind; it is not continuous with thixotropy and occurs for an entirely different reason. No means, however, of defining dilatency quantitatively has yet been devised.

Another method of differentiating suspensions from liquids is by use of the fact that many liquids show a

yield point and act elastically at low stresses. Suspensions of particles which tend to flock or suspensions of high solid concentration show this property to be due to the formation of a scaffold or mesh, as stated by McDowell and Usher[2] and Hauser and Reed,[3] or simply to interparticle forces.

The following factors, in general, are important in influencing the flow characteristics of a suspension: (1) concentration of solid (expressed as volume of solid based on the total volume), (2) mean size of suspended particle, (3) particle-size distribution, (4) shape of particle, (5) surface forces influencing interaction between particle and liquid or two adjacent particles, and (6) viscosity of suspending medium.

Suspensions of spheres in a liquid have been studied by a number of experimenters.[4] All of the spheres, however, were of larger size and would not be comparable with clay particles and they were not generally in aqueous suspensions. Einstein[5] has proposed a theoretical law which relates the viscosity of the suspension with the concentration of the suspended spheres and which may be stated as follows:

$$\eta_s = \eta_l (1 + kC)$$

This law is based on the following assumptions: (*a*) spherical particles, (*b*) dilute suspension, (*c*) no charge on the particle, and (*d*) no adhering water hull. The constant, k, in this equation is 2.5, which holds experimentally for low concentrations, but it fails at concentrations over a few percentage.

Hatschek[6] proposed a theoretical law of the same form as Einstein's for a suspension of spheres but with a constant of 4.5. Experimental conformation again can be obtained only with dilute suspensions.

Arrhenius[7] had previously proposed an exponential law as follows:

$$\eta_s = \eta_l e^{kC}$$

k = a constant.

If C is plotted on the linear scale and η on the logarithmic scale of semilogarithmic paper, a straight line obviously should result with a slope proportional to k. Weltmann and Green[8] state that a modification of this law agrees with quite concentrated suspensions of pigments in oils but does not cover dilute suspensions. The law does not hold at all for kaolinite suspensions.

Some experimental work has been done with suspended quartz particles in water, and the effect of size and concentration has been studied although really monodisperse systems again have not been available. This particular system, however, is interesting in showing clearly the peculiarities of dilatency. Freundlich and Röder[9] found that dilatency occurred in such a system only in a range of 42 to 45% by weight of solids when the particle size was 1 to 5 microns. The narrow range of solid concentration to produce dilatency has been confirmed with other materials although the particle volume in clays is considerably lower. Dilatency has been explained as a change in type of packing under motion. In other words, when the suspension is quiet the particles settle down into a close-packed system with a low pore volume so that there is sufficient water to form a lubricating layer; under motion, the particles are disordered and produce a more or less open structure so that the water is insufficient to carry the particles; a kind of continuous network is formed, producing high apparent viscosity. Further studies on dilatency are needed before complete explanation can be offered. Thixotropic materials in general have a larger sedimentation volume than dilatent ones.

The type of liquid medium in the suspension is quite important in some cases. Although the present study is concerned only with water as a liquid, work has been carried out on nonpolar liquids with interesting results. Freundlich and Jones[10] showed that the flow properties of a suspension of quartz in various liquids is considerably altered with the various types of liquid. For example, quartz in water shows dilatency, whereas in carbon tetrachloride it is thixotropic, but much more experimental work is necessary to give data from which definite conclusions can be based. The question of electrolytes added to water will be considered with sodium hydroxide used as a deflocculating agent; this has a pronounced effect on the viscosity and will be discussed later.

III. Flow Properties in Suspensions of Anisotropic Particles

Suspensions of anisotropic particles show characteristics similar to those of isotropic particles but with some differences. In the first place, the apparent viscosity varies with the rate of shear but generally to a much greater extent than with the isotropic particles; the latter therefore are highly thixotropic. The anisotropic particles in suspension usually show a relatively high yield point because it is easier to form a rigid network than with the isotropic particles. Whether or not a definite lower limit in concentration exists below which there is no yield point cannot be determined from

[2] C. M. McDowell and F. L. Usher, "Viscosity and Rigidity in Suspensions of Fine Particles: I, Aqueous Suspensions," *Proc. Roy. Soc.*, **A131**, 409–27 (1931); "II, Nonaqueous Suspensions," *ibid.*, pp. 564–76 (1931).

[3] E. A. Hauser and C. E. Reed, "Studies in Thixotropy: II, Thixotropic Behavior and Structure of Bentonite," *Jour. Phys. Chem.*, **41**, 911–34 (1937).

[4] F. Eirich, M. Bunzl, and H. Margaretha, "Viskosität Suspensionen und Lösungen: IV, Kugelsuspensionen" (Viscosity of Suspensions and Solutions: IV, Viscosity of Globular Suspensions), *Kolloid Z.*, **74**, 276–85 (1936); *Ceram. Abs.*, **15** [7] 220 (1936).

[5] A. Einstein, "Neue Bestimmung der Moleküldimensionen," *Ann. Physik*, **19**, 289–306 (1906).

[6] (*a*) Emil Hatschek, "Viskosität der Dispersoide," *Kolloid Z.*, **7**, 301–304 (1910); *ibid.*, **8**, 34–39 (1911).
(*b*) Emil Hatschek "General Theory of Viscosity of Two-Phase Systems," *Trans. Faraday Soc.*, **9**, 80–92 (1913).

[7] Svante Arrhenius, "Innere Reibung verdünnter wässeriger Lösungen," *Z. physik. Chem.*, **1**, 285 (1887).

[8] R. N. Weltmann and H. Green, "Rheological Properties of Colloidal Solutions, Pigment Suspensions, and Oil Mixtures," *Jour. Applied Phys.*, **14**, 569–76 (1943).

[9] H. Freundlich and H. L. Röder, "Dilatency and Its Relation to Thixotropy," *Trans. Faraday Soc.*, **34**, 308–16 (1938).

[10] H. Freundlich and A. D. Jones, "Sedimentation Volume, Dilatency, Thixotropic, and Plastic Properties of Concentrated Suspensions," *Jour. Phys. Chem.*, **40**, 1217–36 (1936).

the present work. With a more sensitive apparatus, yield points may perhaps be determined to still lower values of concentration.

Elongated ellipsoidal particles in suspensions have been treated from the hydrodynamic point of view by Jeffrey,[11] who arrived at an equation of the Einstein form but only for dilute suspensions. Eirich and his co-workers[12] experimented with rods of varying diameter-to-length ratios in dilute nonaqueous suspensions. The rate of rotation of particles of this type depends on torque produced by the velocity gradient. This rotation is resisted by viscous forces acting on portions of the particle moving at a speed not corresponding with its position in the liquid. As previously described, isotropic particles rotate at a constant speed, but the anisotropic particles will rotate in a nonuniform manner because the velocity gradient will act on the particle with more effect when its axis is normal to the direction than when it is parallel to it.

IV. New Expression Relating Viscosity of Suspension with Concentration of Solid

The many expressions previously suggested for the relationship between η_s and C have restricted themselves to dilutions where there is no interaction between the particles. Because suspensions are of little interest to the ceramist, a new relation is proposed that covers not only the dilute suspensions but also those of higher concentrations in the range of casting slips. Although the form of the equation is based on hydrodynamic relations, the constants are entirely empirical.

The magnitude of the viscosity of a suspension is obviously the sum of three independent effects, which may be expressed (*a*) by the part due to the viscosity of the liquid medium, formula (1); (*b*) by the part caused by the sum of the individual particles or groups of particles as they rotate in the velocity gradient of the liquid medium, formula (2); and (*c*) by the part due to the collision or interference of the particles (or groups) with each other, formula (3).

$$(1 - C)\eta_l \tag{1}$$

$C = 0$.
$\eta_s = \eta_l$.

$$k_1 C \tag{2}$$

C is proportional to number of particles, N.
k_1 dimensions must be those of viscosity for C is a ratio.
k_1 depends on size of particle (or group), shape, and surface activity.

$$k_2 C^n \tag{3}$$

k_2 has dimensions of viscosity and depends on size, shape, and surface activity of particles (or groups).
n depends on surface activity but not on mean particle size.

Equation (4) gives the complete relation expressing the viscosity of a suspension.

$$\eta_s = \eta_l (1 - C) + k_1 C + k_2 C^n \tag{4}$$

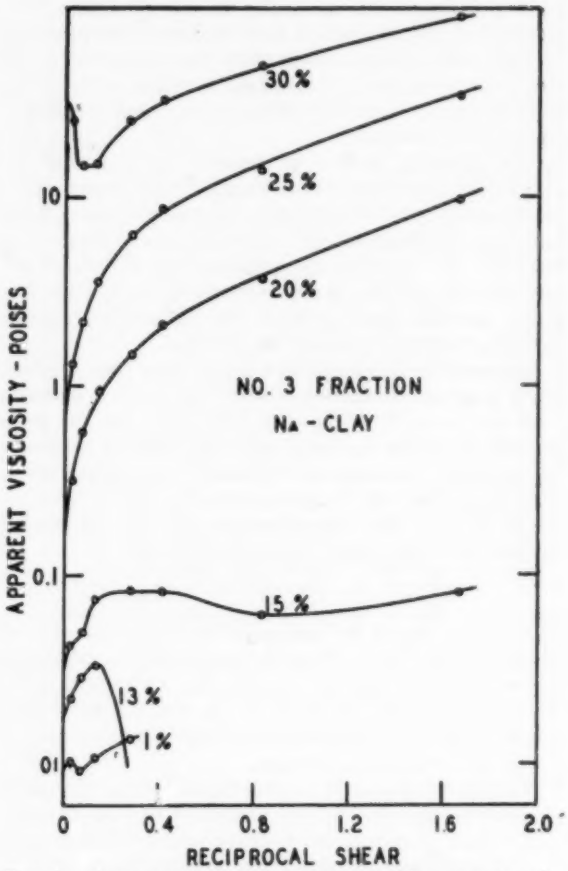

FIG. 5.—Apparent viscosity of slips at different rates of shear.

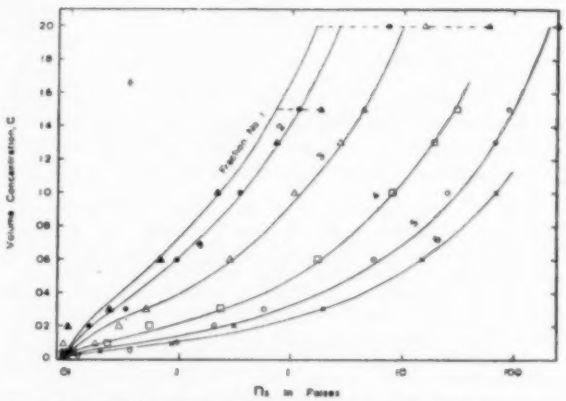

FIG. 6.—Relation between viscosity and volume concentration of solids for six fractions containing H kaolinite.

This relation, equation (4), should apply to all concentrations up to the point where the particles pack close enough for dilatency to start. The first and second terms dominate at low values of C and the third one is most important at high values.

[11] G. B. Jeffrey, "Motion of Ellipsoidal Particles Immersed in Viscous Fluid," *Proc. Roy. Soc.*, **A102**, 161–79 (1922).

[12] F. Eirich, H. Margaretha, and M. Bunzl, "Viskosität von Suspensionen: VI, Viskosität von Stäbchensuspensionen" (Viscosity of Suspensions and Solutions: VI, Viscosity of Acicular Suspensions), *Kolloid Z.*, **75**, 20–37 (1936); *Ceram. Abs.*, **15** [7] 220 (1936).

V. Experimental Confirmation of Equation (4)

This laboratory was fortunate in having six monodisperse fractions of kaolinite of high purity (Table I). These particles, in all sizes, are flat hexagonal plates. The diameter-to-thickness ratio of 8 was obtained from optical density measurements in the electron microscope and by the settling velocity for the finest fraction, and there is reason to believe that this ratio holds approximately for the other fractions.

These fractions were tested after long electrodialysis to produce a pure H kaolinite and with added NaOH to produce a Na kaolinite. The fact that these suspensions are highly purified makes them excessively sensitive to minute quantities of dissolved material in the water such as solution from the container and CO_2 from the air. This largely accounts for the scattering of the points on the curves in Figs. 5 to 11.

The viscosity measurements were made in the modified MacMichael viscosimeter as described by Johnson and Norton.[13] The slips were made up with distilled water and just the proper amount of sodium hydroxide to give complete deflocculation. All of the slips were agitated in a shaking machine for one hour, allowed to age for 24 hours, agitated one additional hour, and tested at once. Complete flow data for all of the fractions tested are given in the Appendix.

The discussion of the flow data will be clarified by considering the various influences which are acting on the viscosity coefficient. One of the most important of these is the rate of shear strain, and a typical set of curves is shown in Fig. 5. It is evident that there is a general rapid increase in apparent viscosity coefficient as the rate of shear strain is decreased except in very dilute suspensions where the viscosity coefficient changes little with the rate of shear strain. At the high concentrations, a drop in viscosity coefficient is noted, which indicates dilatency in this particular region. It was also noted that in some of the curves of this type a slight dip occurred at a rate of shear-strain value of approximately 0.3. This dip is small, but it is difficult to give a reasonable explanation of it unless it is due to some resonance set up at this particular rotational speed and thickness of suspension. It is difficult to see how it can actually be a function of the suspension as it occurs at all concentrations and all particle sizes at roughly the same rate of shear strain. It is interesting to note that Richardson,[14] who shows similar curves on clay suspensions, obtains a similar kink and at about the same rate of shear strain. It was necessary to plot Fig. 5 on semilogarithmic paper in order to get all of the curves on one sheet, because of the great changes in viscosity coefficient. The thixotropic coefficient was determined, however, on a separate linear plot as previously described. The general theory of Goodeve,[1] that the basic coefficient of viscosity is represented by a condition where all the particles are acting independently, does not appear to be confirmed by these results. There is a considerable difference between the basic viscosity value of a given suspension, depending on whether it is flocculated or deflocculated, and naturally there should be no great difference if the particles were entirely separate. There is also good reason to believe that the deflocculated suspensions do not form particle groups at any rate of shear. This means that a linear extrapolation to infinite shear is not justified.

TABLE I

PROPERTIES OF KAOLINITE SUSPENSIONS

Fraction No.	Avg. diam. (μ)	Specific surface (sq. m./gm.)
1	10.0	0.78
2	4.4	1.75
3	2.5	3.10
4	0.95	8.17
5	0.52	14.5
6	0.28	28.5

Values of η_s for the six H-kaolinite fractions plotted on semilogarithmic paper are shown in Fig. 6. The corresponding curves are plotted from equation (4) with the constants given in Table II.

Except for the two coarsest fractions at the high concentrations where dilatency starts, the experimental points coincide with the theoretical values within the experimental error. For the first time, therefore, a relation has been found which agrees with the experimental results over the whole range of concentration up to the point of dilatency, covering a viscosity range in this case of 10,000 to 1. Twenty to thirty volume percentage of solids may seem to be a low maximum value, but the upper limit is much lower in a monodisperse system than in the ordinary suspensions having a large size range.

The six fractions of Na kaolinite, if plotted in the same way as was done for the H fractions, will show little because the points for the various fractions are rather closely intermixed. In other words, particle size has little effect. The mean value of the fractions may be expressed by equation (4) with

$$n = 3.$$
$$k_1 = 0.08$$
$$k_2 = 7.5$$

In the deflocculated system, however, the particles may reasonably be assumed to be individuals, in which case the center-to-center distance may be computed as based on tetrahedral packing.* These values are given in the Appendix in Table V. It is readily seen that the concentration, C, is proportional to the cube of the spacing (d^3). Equation (4) may then be rewritten as equation (5).

$$\eta_s = (1 - C)\eta_1 + k_1{}'d^3 + k_2{}'d^{12} \qquad (5)$$

The experimental values of η_s versus d for the six fractions are plotted in Fig. 7. These values fall on the curves plotted from equation (5) with the constants given in Table II.

[13] A. L. Johnson and F. H. Norton, "Fundamental Study of Clay: I, Preparation of Purified Kaolinite Suspension," *Jour. Amer. Ceram. Soc.*, **24** [2] 64–69 (1941).

[14] E. G. Richardson, "Some Physical Properties of Clay," *Trans. Brit. Ceram. Soc.*, **38** [6] 359–77 (1939); *Ceram. Abs.*, **18** [11] 311 (1939).

* The suggestion of tetrahedral packing was made by P. D. Johnson of the Ceramic Laboratory.

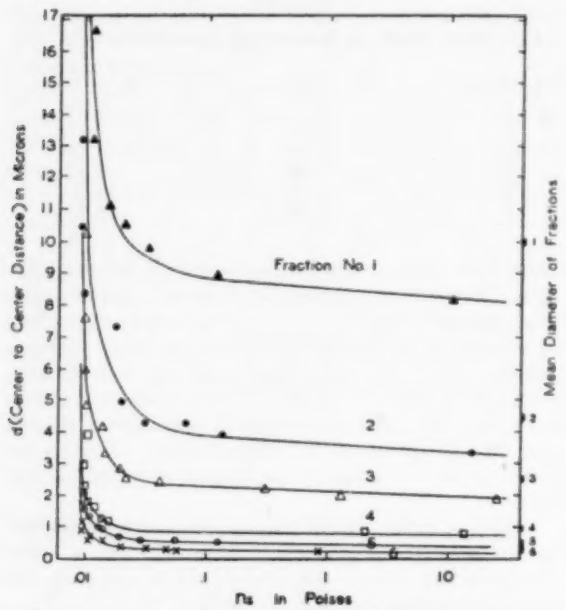

FIG. 7.—Relation between viscosity and center-to-center distance of particles of six fractions containing Na kaolinite.

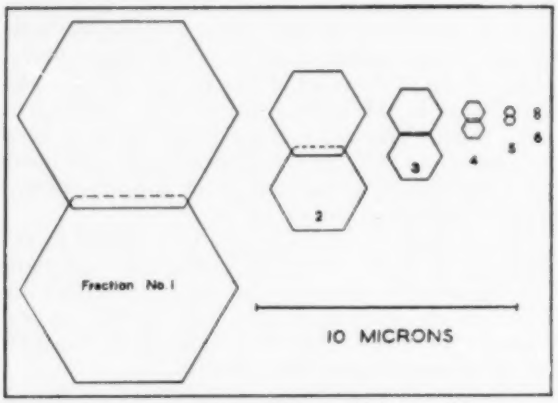

FIG. 8.—Relative spacing of Na-kaolinite particles when η_s is equal to 3 poises.

A relatively small change occurs in k_1^1 with particle size; the change in k_2^1 is very large, which indicates the importance of the interference effect. The value of n is very large, causing the viscosity to change as the 36th power of d. Although n is a constant for all the fractions tested, it might be expected to vary somewhat with other clays or bodies.

One significant fact brought out by these curves is that the last term in equation (5) begins to assume importance with each fraction when the center-to-center distance approaches the particle diameter. This result indicates clearly that the surface forces in the deflocculated state do not extend any great distance into the water and that the increase in viscosity is caused mainly by mechanical interference of the revolving or sliding plates. Figure 8 shows the relative spacing of the various-sized particles for a constant viscosity.

TABLE II

CONSTANTS FOR EQUATIONS (4), (5), (6), (7), AND (8)

Fraction No.	k_1	k_2	n
	Constants for equation (4)		
1	0.20	200	3
2	.25	330	3
3	.35	1250	3
4	.45	7900	3
5	.50	31,000	3
6	.55	69,000	3
	k_1^1	k_2^1	n
	Constants for equation (5)		
1	10	1.1×10^{33}	12
2	18	1.5×10^{19}	12
3	0.26	0.5×10^{11}	12
4	0.012	2.0×10^{-5}	12
5	0.004	0.5×10^{-14}	12
6	0.007	1.0×10^{-25}	12
	k_3	k_4	n
	Constants for equation (6)		
1	1	6.2×10^2	3
2	1	6.2×10^2	3
3	2	3.4×10^4	3
4	5	1.8×10^5	3
5	7	5×10^5	3
6	10	16×10^5	3
	k_3^1	k_4^1	n
	Constants for equation (7)		
1	800	10^{30}	12
2	2	10^{19}	12
3	1	10^9	12
4	0.7	1	12
5	0.05	10^{-13}	12
6	0.006	10^{-28}	12
	k_5		n
	Constants for equation (8)		
1	0.6		3
2	2.5		3
3	11.0		3
4	68		3
5	210		3
6	1050		3

VI. Mechanism of Thixotropy

Thixotropy is the rate of change of viscosity as the rate of shearing strain varies and has the units of intensity of stress. Because the liquid medium itself has no thixotropic properties, it might be expected that the thixotropy of the suspension could be expressed by equation (6).

$$\theta = k_3 C + k_4 C^n \qquad (6)$$

The values of thixotropy for the six fractions are plotted in Fig. 9, and the corresponding curves plotted from (6) with constants are given in Table II.

The agreement between the experimental and computed values is good in most cases in spite of the fact that θ is derived from the difference of two small numbers and has less precision than η_s.

Values of θ for the Na-kaolinite suspensions, as for the viscosity, fulfill equation (7). The values for the constants are given in Table II.

$$\theta = k_3^1 d^3 + k_4^1 d^{3n} \qquad (7)$$

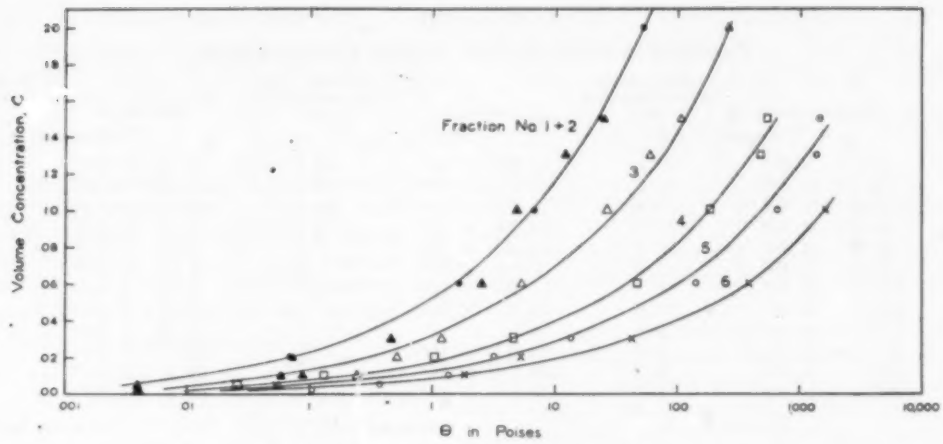

FIG. 9.—Thixotropy of H-kaolinite fractions.

These constants cannot be determined as precisely as the others because the experimental values are small and the points are rather scattered.

The change of thixotropy with particle size is caused almost entirely by the interference or collision resistance and not by the resistance offered by the individual particle. It is also interesting to note that in all cases, at least within the experimental error, the value of thixotropy is 18 times the value for the corresponding viscosity. In other words, the ratio of viscosity to thixotropy is a constant for these suspensions. Because the units of viscosity are $ML^{-1}T^{-1}$ and the units of thixotropy are $ML^{-1}T^{-2}$, the unit of thixotropy divided by viscosity will be T^{-1}. This value, T^{-1}, will therefore be a constant for all of the systems under discussion, but just what significance this has is not clear at the present time. The value of T of 0.05 second may possibly represent the time required to reach a new equilibrium state after a change in shearing rate.

There is still no satisfactory explanation of thixotropy. The school which believes thixotropy is due to a changing size group with rate of shear offers a possible explanation for flocculated systems, but this concept is not sufficiently broad to cover deflocculated systems where it is known that a majority of the particles act as individuals. There is reason to believe that thixotropy is not present in suspensions of spheres, but no published measurements that are available have been sufficiently precise to determine very small values if they were present. It may be said, however, that the majority of suspensions show thixotropy so that the lack of this property in a suspension would be an unusual occurrence. It is hoped that when the work being carried out in this laboratory at the present time is completed a more thorough understanding of thixotropy will be gained, and this question will be treated thoroughly in a forthcoming paper.

VII. Yield Point

The yield point or shear strength of the gel at zero rate of shear strain will evidently be proportional to the active surface area of the particles, their surface

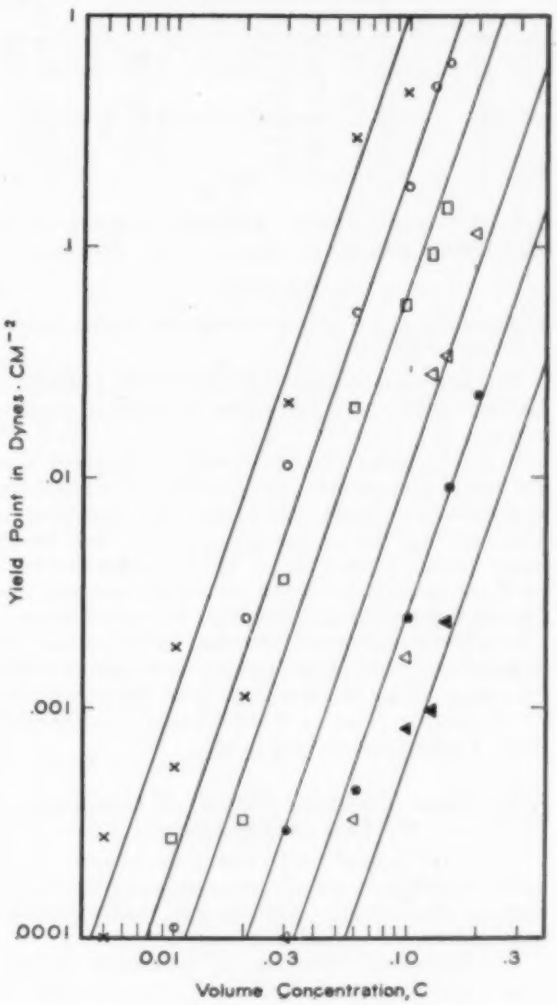

FIG. 10.—Relation between yield point and volume concentration of solids for six fractions containing H kaolinite.

TABLE III

PARTICLES IN SUSPENSIONS OF VARYING CONCENTRATIONS

Volume concentration	Particles/cc.	Center-center particle distance (μ)	Particles/cc.	Center-center particle distance (μ)	Particles/cc.	Center-center particle distance (μ)
	Fraction No. 1		Fraction No. 2		Fraction No. 3	
0.002	2.05×10^{7}	40.9	0.239×10^{9}	18.1	0.130×10^{10}	10.2
.005	5.14×10^{7}	30.1	0.598×10^{9}	13.3	0.328×10^{10}	7.6
.01	10.2×10^{7}	23.8	1.195×10^{9}	10.5	0.652×10^{10}	6.0
.02	20.2×10^{7}	19.0	2.39×10^{9}	8.4	1.30×10^{10}	4.8
.03	30.5×10^{7}	16.6	3.59×10^{9}	7.3	1.95×10^{10}	4.2
.06	61.5×10^{7}	13.2	7.18×10^{9}	5.8	3.91×10^{10}	3.3
.10	102×10^{7}	11.1	11.95×10^{9}	4.9	6.52×10^{10}	2.8
.13	133×10^{7}	10.6	15.5×10^{9}	4.5	8.47×10^{10}	2.5
.15	154×10^{7}	9.8			9.78×10^{10}	2.4
.20	205×10^{7}	8.9	23.9×10^{9}	3.9	13.0×10^{10}	2.2
.25	256×10^{7}	8.2	29.9×10^{9}	3.6	16.3×10^{10}	2.1
.30	306×10^{7}	7.7	35.9×10^{9}	3.4	19.5×10^{10}	1.9
	Fraction No. 4		Fraction No. 5		Fraction No. 6	
0.002	0.238×10^{11}	3.9	0.145×10^{12}	2.1	0.093×10^{13}	1.1
.005	0.595×10^{11}	2.9	0.362×10^{12}	1.6	0.228×10^{13}	0.84
.01	1.19×10^{11}	2.3	0.724×10^{12}	1.3	0.465×10^{13}	0.67
.02	2.38×10^{11}	1.8	1.45×10^{12}	0.99	0.930×10^{13}	0.53
.03	3.56×10^{11}	1.6	2.17×10^{12}	0.87	1.38×10^{13}	0.51
.06	7.13×10^{11}	1.3	4.34×10^{12}	0.69	2.79×10^{13}	0.37
.10	11.9×10^{11}	1.1	7.24×10^{12}	0.59	4.65×10^{13}	0.31
.13	15.4×10^{11}	0.97	9.41×10^{12}	0.53	6.04×10^{13}	0.30
.15	17.8×10^{11}	0.90	10.8×10^{12}	0.51	6.98×10^{13}	0.27
.20	23.8×10^{11}	0.84	14.5×10^{12}	0.46	9.30×10^{13}	0.25
.25	29.7×10^{11}	0.74	18.1×10^{12}	0.43	11.6×10^{13}	0.23
.30	35.6×10^{11}	0.73	21.7×10^{12}	0.40	13.9×10^{13}	0.22

activity, and their shape. Equation (8) would then be expected to occur.

$$YP = k_s C^n \qquad (8)$$

k_s (dynes/sq. cm.) is related to shape and surface activity (attractive forces).

This relation is shown to hold true for the H-kaolinite fractions in Fig. 10. The values of k_s and n are given in Table II.

It will be noted that k_s increases much faster than the actual particle area, but it should be remembered that the contact area is only a small fraction of the total area and that the smaller particles may well have a larger relative contact area. The term "contact area" does not necessarily imply actual contact but may mean a slight separation stabilized by surface forces.

It is particularly interesting that the theoretical and actual values show no discrepancy even up to the highest concentration because there is no disturbing effect of dilatency. None of the Na-kaolinite suspensions showed a measurable yield point.

VIII. More Complete Picture of Mechanism of Flow of Suspensions

It may be instructive to take a suspension and observe the effect of varying separately (1) the concentration, (2) rate of shear, (3) particle size, and (4) surface activity.

The influence of concentration has already been discussed and found to follow closely equations (4), (5), (6), and (7) for the viscosity, thixotropy, and yield point, respectively.

The effect of particle size on viscosity is marked in the H-kaolinite suspensions but much less evident in the Na-kaolinite suspensions. For example, from the coarsest to the finest fraction of H kaolinite, the value of k_1 increases only slightly from 0.20 to 0.55, whereas k_2 increases from 200 to 69,000. This result indicates that the contribution from the individual particles varies little from one fraction to another, but energy absorbed in collision increases enormously as the particle size decreases, perhaps because of the greater surface area in the fine sizes. The values for k_1 and k_2 of the Na-kaolinite suspensions, however, are little influenced by size. This is undoubtedly due to the complete, or almost complete, elimination of the attractive forces in the Na kaolinite so that the plates or groups bounce off each other with little energy loss.

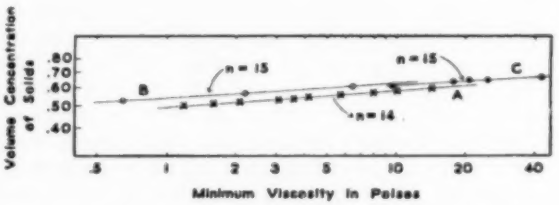

FIG. 11.—Relation between actual and calculated viscosity of ceramic casting slips.

The effect of surface activity is marked, especially in the fine fractions. A viscosity change of 2000 times is possible here simply by replacing the H^+ counter ions by Na^+. The previous paragraph shows that most of this change is caused by changes in interference effects. A somewhat similar change occurs in the yield point of the fine fraction, which is high in the H-kaolinite suspension but zero in the Na-kaolinite suspension.

IX. Application to Casting Slips

Because casting slips are always of such high concentration that only the last term in equation (4) is of any importance, equation (9) may be used.

$$\eta_s = k_2 C^n \qquad (9)$$

A series of minimum viscosity values for a commercial sanitary-ware casting slip for various values of solid concentration has been plotted on logarithmic paper, curve *A*, Fig. 11. The resulting straight line has a slope of 14. This slip, therefore, exactly conforms to the following relation and any intermediate value may be readily computed.

$$\eta_s = 2100 \cdot C^{14}$$

Curve *B*, Fig. 11, shows values of viscosity for a semivitreous casting slip. A straight line again occurs, and the relation is as follows:

$$\eta_s = 1300 \cdot C^{16}$$

In curve *C*, Fig. 11, the values of viscosity are plotted for a special casting slip, which may be represented by

$$\eta_s = 1500 \cdot C^{15}$$

In this way, it is only necessary to find the constants for a given slip by a measurement at two conditions and then all others can readily be calculated by equation (9) or determined graphically on a logarithmic plot.

X. Summary

It has been shown that the viscosity of a suspension of kaolinite in water is due to three additive effects, namely, the contribution of (1) the liquid, (2) the separate particles, and (3) the interference between particles. This relation, unlike those previously presented, covers the entire range of concentration up to the point of dilatency. A few cases indicate that this relation may be used with commercial casting slips so that when the viscosity is known for one specific gravity it may be computed for others.

Appendix 1: Calculation of Particle Numbers and Particle Spacing in a Suspension

Table III shows the number of particles to be found in suspensions of various concentrations. These calculations were based on the assumption that the kaolinite particle is a flat disk with a 1 to 8 ratio of thickness to diameter. The volume of a single disk is given in equation (10).

$$V = \pi r^2 T \qquad (10)$$

V = volume (cc.).
r = radius (cm.).
T = thickness (cm.).

A sample calculation will illustrate the procedure. For coarsest fraction No. 1, the average diameter is 10.0 micron; the thickness of the disk therefore would be 10.0 divided by 8 or 1.25 microns. The volume of a single particle follows.

$$r = 5.0 \times 10^{-4} \text{ cm.}$$
$$T = 1.25 \times 10^{-4} \text{ cm.}$$
$$V = 3.14\ (5.0 \times 10^{-4})^2\ (1.25 \times 10^{-4})$$
$$V = 97.5 \times 10^{-12} \text{ cc.}$$

The number of particles in 1 cc. volume is the reciprocal of 97.5×10^{-12} or 10.2×10^9 particles; the number of particles in 1 cc. of a 0.01 concentration suspension by volume then is $10.2 \times 10^9 \times 0.01$ or 10.2×10^7 particles.

The center-to-center distance between particles in the various suspensions may be determined as follows: A 1-cc. suspension is assumed, containing N particles in tetrahedral packing, and d is assumed to be the distance between particles. With tetrahedral packing, the distance between particles will be the same in all directions and consequently more closely approaches the actual arrangement of particles in a suspension.

The spacing along one row is d, and the number of particles in one row is $1/d$. Considering a sheet where the distance between rows is the altitude of an equilateral triangle with a side d, the altitude is $d\frac{\sqrt{3}}{2}$ and the number of rows is $\frac{1}{d\frac{\sqrt{3}}{2}}$. If the volume is assumed, wherein the distance between layers is the altitude of a tetrahedron or $d\sqrt{\frac{2}{3}}$ and the number of rows is $\frac{1}{d\sqrt{\frac{2}{3}}}$, equation (11) will be obtained.

$$N = \frac{1}{d} \times \frac{1}{d\sqrt{\frac{3}{2}}} \times \frac{1}{d\sqrt{\frac{2}{3}}} = \frac{1}{\frac{\sqrt{2}}{2} d^3} = \frac{1}{0.71 d^3} =$$

$$1.4 + d^{-3} \qquad (11)$$

$$d = 1.12 N^{-1/3}$$

Using the No. 1 fraction, the number of particles, N, in 1 cc. of a 0.01 concentration suspension from Table III is 10.2×10^7. Substituting in equation (11), d, the center-to-center distance, is as follows:

$$d = \frac{1.12}{\sqrt[3]{10.2 \times 10^7}} = 23.9 \times 10^{-4} \text{ cm.} = 23.9 \text{ u.}$$

Appendix 2: Calculation of Viscosity and Yield Point

Table IV gives the data obtained on the various suspensions with the modified MacMichael viscosimeter. The rate of shear is obtained by the following relation:

$$\frac{dv}{dr} = \frac{2\pi r_2 S}{r_2 - r_1}$$

(Appendix 2 concluded on p. 164)

TABLE IV

DATA ON VARIOUS SUSPENSIONS WITH MODIFIED MACMICHAEL VISCOSIMETER

Concentration	Yield point (dyne·cm.$^{-2}$)	Torque (gm.-cm.)	Apparent viscosity coeff. (poise)	Shear strain (rate)	Thixotropy coeff.	Yield point (dyne·cm.$^{-2}$)	Torque (gm.-cm.)	Apparent viscosity coeff. (poise)	Shear strain (rate)	Thixotropy coeff.
		No. 1 fraction (H kaolin)					No. 2 fraction (H kaolin)			
0.002		0.0109	0.0089	30.1	0.003		0.0113	0.0092	30.1	0.0
		0.0055	0.0090	15.0			0.0055	0.0090	15.0	
		0.0032	0.0104	7.5			0.0025	0.0089	7.5	
.005		0.0109	0.0089	30.1	0.003		0.0120	0.0098	30.1	0.0
		0.0055	0.0090	15.0			0.0052	0.0089	15.0	
		0.0032	0.0104	7.5			0.0030	0.0098	7.5	
.01		0.0112	0.0091	30.1	0.088		0.0131	0.0107	30.1	0.06
		0.0074	0.0121	15.0			0.0067	0.0109	15.0	
		0.0046	0.015	7.5			0.0041	0.0134	7.5	
.02		0.0122	0.0100	30.1	0.006	0.06	0.0188	0.0153	30.1	0.074
		0.0060	0.0098	15.0			0.0097	0.0178	15.0	
		0.0034	0.0111	7.5			0.0065	0.0212	7.5	
.03		0.030	0.024	30.1	0.147	0.15	0.041	0.033	30.1	0.47
		0.018	0.029	15.0			0.030	0.049	15.0	
		0.014	0.046	7.5			0.026	0.085	7.5	
		0.010	0.068	3.6			0.019	0.129	3.6	
		0.007	0.071	2.4			0.016	0.164	2.4	
		0.002	0.041	1.2			0.010	0.204	1.2	
		0.001	0.081	0.6			0.008	0.65	0.6	
.06		0.085	0.069	30.1	1.26	0.23	0.115	0.094	30.1	1.65
		0.069	0.112	15.0			0.092	0.150	15.0	
		0.055	0.179	7.5			0.080	0.261	7.5	
		0.044	0.299	3.6			0.073	0.496	3.6	
		0.039	0.398	2.4			0.066	0.67	2.4	
		0.027	0.551	1.2			0.053	1.06	1.2	
		0.018	1.46	0.6			0.030	2.45	0.6	
.10	3.67	0.270	0.220	30.1	4.96	1.32	0.425	0.346	30.1	6.85
		0.239	0.389	15.0			0.355	0.579	15.0	
		0.207	0.675	7.5			0.310	1.01	7.5	
		0.170	1.16	3.6			0.295	2.00	3.6	
		0.165	1.68	2.4			0.280	2.86	2.4	
		0.160	3.26	1.2			0.205	4.18	1.2	
		0.075	6.08	0.6			0.060	4.89	0.6	
.13	5.14	0.92	0.750	30.1	12.35					
		0.72	1.17	15.0						
		0.60	1.96	7.5						
		0.57	3.88	3.6						
		0.50	5.10	2.4						
		0.40	8.16	1.2						
.15	7.05	2.24	1.83	30.1	25.3	4.7	1.4	1.14	30.1	24.1
		1.65	2.69	15.0			1.2	1.96	15.0	
		1.2	3.91	7.5			1.08	3.52	7.5	
		1.2	8.16	3.6			0.94	6.39	3.6	
		1.2	12.2	2.4			0.82	8.36	2.4	
		0.8	16.3	1.2			0.54	11.0	1.2	
							0.18	14.7	0.6	
.20	288	72.4	59.0	30.1	0.0	11.75	9.0	7.34	30.1	52.6
		35.4	57.7	15.0			5.6	9.13	15.0	
		18.2	59.3	7.5			4.25	13.9	7.5	
		12.5	85.0	3.6			3.5	23.8	3.6	
							2.2	22.4	2.4	
							1.1	22.4	1.2	
							0.5	40.7	0.6	

TABLE IV (*continued*)

Concentration	Yield point (dyne·cm.$^{-2}$)	Torque (gm.-cm.)	App. viscosity coeff. (poise)	Shear strain (rate)	Thixotropy coeff.	Yield point (dyne·cm.$^{-2}$)	Torque (gm.-cm.)	App. viscosity coeff. (poise)	Shear strain (rate)	Thixotropy coeff.
		No. 3 fraction (H kaolin)					No. 4 fraction (H kaolin)			
0.002		0.0124	0.0101	30.1	0		0.0122	0.0100	30.1	0.0
		0.0054	0.0089	15.0			0.0057	0.0093	15.0	
		0.0028	0.0091	7.5			0.0033	0.0108	7.5	
		0.0014	0.0095	3.6			0.0020	0.0136	3.6	
		0.0010	0.0102	2.4			0.0010	0.0102	2.4	
		0.0006	0.0122	1.2			0.0006	0.0122	1.2	
.005		0.0132	0.0108	30.1	0.065		0.0138	0.0112	30.1	0.026
		0.0080	0.0130	15.0			0.0074	0.0121	15.0	
		0.0048	0.0157	7.5			0.0053	0.0173	7.5	
		0.0036	0.0244	3.6			0.0039	0.0265	3.6	
		0.0026	0.027	2.4			0.0025	0.0255	2.4	
		0.0013	0.027	1.2			0.0017	0.0347	1.2	
.01		0.0219	0.0178	30.1	0.253	1.47	0.0280	0.0228	30.1	0.135
		0.0162	0.0264	15.0			0.0168	0.0274	15.0	
		0.0107	0.035	7.5			0.0130	0.0424	7.5	
		0.0063	0.043	3.6			0.0105	0.0712	3.6	
		0.0051	0.052	2.4			0.0078	0.0796	2.4	
		0.0043	0.088	1.2			0.0055	0.112	1.2	
.02	0.03	0.035	0.029	30.1	0.53	1.76	0.0659	0.0536	30.1	1.06
		0.029	0.047	15.0			0.0549	0.0895	15.0	
		0.022	0.072	7.5			0.0456	0.149	7.5	
		0.017	0.116	3.6			0.0380	0.258	3.6	
		0.014	0.143	2.4			0.0363	0.371	2.4	
		0.012	0.245	1.2			0.0252	0.514	1.2	
		0.010	0.810	0.6						
.03	0.06	0.062	0.051	30.1	1.18	1.88	0.288	0.235	30.1	4.59
		0.056	0.091	15.0			0.240	0.391	15.0	
		0.049	0.160	7.5			0.198	0.645	7.5	
		0.040	0.272	3.6			0.170	1.16	3.6	
		0.034	0.347	2.4			0.170	1.73	2.4	
		0.025	0.510	1.2			0.139	2.84	1.2	
		0.010	0.810	0.6			0.093	7.58	0.6	
.06	0.18	0.348	0.284	30.1	5.35	10.26	2.13	1.74	30.1	47.0
		0.286	0.466	15.0			2.05	3.34	15.0	
		0.260	0.848	7.5			1.89	6.16	7.5	
		0.220	1.50	3.6			1.65	11.2	3.6	
		0.210	2.14	2.4			1.58	16.1	2.4	
		0.15	3.06	1.2			0.49	10.0	1.2	
		0.064	5.18	0.6			0.44	35.6	0.6	
.10	8.65	1.32	1.08	30.1	27.1	29.35	9.8	7.99	30.1	185.7
		1.23	2.00	15.0			8.8	14.3	15.0	
		1.15	3.75	7.5			8.4	27.4	7.5	
		1.05	7.14	3.6			4.0	27.2	3.6	
		0.945	9.64	2.4			3.0	30.6	2.4	
		0.415	8.47	1.2			2.4	49.0	1.2	
		0.310	25.1	0.6						
.13	14.7	3.4	2.77	30.1	60.0	49.9	23.4	19.1	30.1	465
		2.95	4.81	15.0			21.4	34.9	15.0	
		2.7	8.80	7.5			15.6	50.9	7.5	
		2.42	16.5	3.6			4.4	29.9	3.6	
		2.00	20.4	2.4			3.7	37.7	2.4	
		0.7	14.3	1.2			3.0	61.2	1.2	
.15	17.6	5.5	4.48	30.1	107	76.4	37.4	30.5	30.1	541
		5.0	8.15	15.0			30.0	48.9	15.0	
		4.55	14.8	7.5			21.4	69.8	7.5	
		3.7	25.2	3.6			5.7	38.7	3.6	
		2.3	23.5	2.4			4.7	47.9	2.4	
		0.7	14.3	1.2						
.20	58.7	19.5	15.9	30.1	271					
		15.4	25.1	15.0						
		11.6	37.8	7.5						
		7.3	49.6	3.6						
		4.5	45.9	2.4						
		1.5	30.6	1.2						

TABLE IV (*continued*)

Concentration	Yield point (dyne·cm.$^{-2}$)	Torque (gm.-cm.)	App. viscosity coeff. (poise)	Shear strain (rate)	Thixotropy coeff.	Yield point (dyne·cm.$^{-2}$)	Torque (gm.-cm.)	App. viscosity coeff. (poise)	Shear strain (rate)	Thixotropy coeff.
		No. 5 fraction (H kaolin)					No. 6 fraction (H kaolin)			
0.002		0.0152	0.0124	30.1	0.106		0.0122	0.010	30.1	0.0
		0.0098	0.0160	15.0			0.0048	0.0089	15.0	
		0.0056	0.182	7.5			0.0034	0.0111	7.5	
		0.0040	0.272	3.6			0.0015	0.0102	3.6	
		0.0031	0.316	2.4			0.0012	0.0122	2.4	
		0.0021	0.428	1.2						
.005		0.0440	0.0359	30.1	0.382	0.032	0.0246	0.020	30.1	0.053
		0.0300	0.0489	15.0			0.0134	0.0218	15.0	
		0.0228	0.0744	7.5			0.0090	0.0294	7.5	
		0.0170	0.1153	3.6			0.0064	0.0435	3.6	
		0.0156	0.159	2.4			0.0056	0.0571	2.4	
		0.0136	0.278	1.2						
.01	0.059	0.108	0.0962	30.1	1.35	0.531	0.105	0.086	30.1	1.85
		0.0870	0.142	15.0			0.0912	0.149	15.0	
		0.0740	0.242	7.5			0.0840	0.274	7.5	
		0.0600	0.407	3.6			0.0726	0.410	3.6	
		0.0528	0.539	2.4			0.0630	0.642	2.4	
		0.0456	0.930	1.2			0.0486	0.992	1.2	
.02	0.129	0.250	0.204	30.1	3.21	0.59	0.370	0.302	30.1	5.26
		0.192	0.313	15.0			0.295	0.481	15.0	
		0.178	0.580	7.5			0.250	0.815	7.5	
		0.164	1.12	3.6			0.195	1.33	3.6	
		0.136	1.39	2.4			0.165	1.68	2.4	
		0.135	2.75	1.2			0.135	2.75	1.2	
		0.077	6.28	0.6			0.105	8.51	0.6	
.03	5.87	0.70	0.571	30.1	13.5	1.17	2.4	1.96	30.1	42.9
		0.63	1.03	15.0			2.1	3.42	15.0	
		0.54	1.76	7.5			1.8	5.87	7.5	
		0.44	2.99	3.6			1.6	10.9	3.6	
		0.42	4.28	2.4			1.2	12.2	2.4	
		0.34	6.93	1.2			0.8	16.3	1.2	
		0.23	18.8	0.6			0.4	32.4	0.6	
.06	27.6	6.8	5.54	30.1	143	15.84	18.4	15.0	30.1	382
		6.4	10.4	15.0			17.2	28.0	15.0	
		6.0	19.6	7.5			15.6	50.9	7.5	
		5.0	33.9	3.6			13.6	92.5	3.6	
		2.24	22.8	2.4			6.4	65.3	2.4	
		1.79	36.5	1.2			4.3	87.7	1.2	
.10	99.8	31.2	25.4	30.1	653	246.5	84	68.5	30.1	1575
		29.2	47.6	15.0			74.8	122	15.0	
		26.0	84.8	7.5			70	228.2	7.5	
		12.5	84.9	3.6			44	299	3.6	
		7.8	79.6	2.4			29.2	297.9	2.4	
		5.4	110.2	1.2			20	408	1.2	
.13	256.0	81.6	66.5	30.1	1360	Not measurable; too viscous				
		69.2	112.8	15.0						
		55.6	181.3	7.5						
		15.0	101.8	3.6						
		12.0	122.4	2.4						
.15	328.5	100.8	88.0	30.1	1440					
		84	136.9	15.0						
		54.4	177.3	7.5						
		23.2	157.5	3.6						
		20.4	208.1	2.4						
		18.6	379.4	1.2						
.20	293.4	305	248.6	30.1	1320					
		180	293.4	15.0						
		110	358.6	7.5						
		60	407	3.6						
		60	612	2.4						
		60	1224	1.2						

TABLE IV (*continued*)

Concentration	Yield point (dyne·cm.$^{-2}$)	Torque (gm.-cm.)	Apparent viscosity coeff. (poise)	Shear strain (rate)	Thixotropy coeff.	Yield point (dyne·cm.$^{-2}$)	Torque (gm.-cm.)	Apparent viscosity coeff. (poise)	Shear strain (rate)	Thixotropy coeff.
		No. 1 fraction (4 me.NaOH)*					No. 2 fraction (4 me. NaOH)*			
.002		0.0108	0.0089	30.1	0.0		0.0109	0.0089	30.1	0.0
		0.0050	0.0089	15.0			0.0048	0.0089	15.0	
		0.0024	0.0089	7.5			0.0022	0.0089	7.5	
.005		0.0110	0.0090	30.1	0.0		0.0112	0.0091	30.1	0.0
		0.0051	0.0089	15.0			0.0051	0.0089	15.0	
		0.0026	0.0089	7.5			0.0024	0.0089	7.5	
.01		0.0115	0.0094	30.1	0.0		0.0113	0.0092	30.1	0.0
		0.0054	0.0089	15.0			0.0053	0.0089	15.0	
		0.0030	0.0098	7.5			0.0024	0.0089	7.5	
.02		0.0117	0.0095	30.1	0.0		0.0120	0.0098	30.1	0.0
		0.0056	0.0091	15.0			0.0050	0.0089	15.0	
		0.0033	0.0126	7.5			0.0032	0.0104	7.5	
.03		0.014	0.0114	30.1	0.0		0.022	0.018	30.1	0.0
		0.006	0.0098	15.0			0.010	0.016	15.0	
		0.001	0.0089	7.5			0.003	0.010	7.5	
							0.001	0.007	3.6	
.06		0.014	0.0114	30.1	0.0		0.022	0.018	30.1	0.0
		0.006	0.0098	15.0			0.010	0.016	15.0	
		0.001	0.0089	7.5			0.002	0.009	7.5	
							0.001	0.009	3.6	
.10		0.019	0.0155	30.1	0.024		0.025	0.020	30.1	0.088
		0.010	0.0163	15.0			0.014	0.023	15.0	
		0.002	0.0089	7.5			0.009	0.029	7.5	
							0.003	0.020	3.6	
							0.002	0.020	2.4	
							0.001	0.020	1.2	
.13		0.026	0.021	30.1	0.059					
		0.014	0.023	15.0						
		0.005	0.016	7.5						
.15		0.040	0.033	30.1	0.088		0.082	0.067	30.1	1.15
		0.022	0.036	15.0			0.065	0.106	15.0	
		0.011	0.036	7.5			0.050	0.163	7.5	
		0.002	0.014	3.6			0.039	0.265	3.6	
		0.001	0.010	2.4			0.032	0.326	2.4	
							0.029	0.592	1.2	
							0.016	1.31	0.6	
.20		0.15	0.122	30.1	0.0		0.0169	0.138	30.1	1.88
		0.074	0.121	15.0			0.124	0.202	15.0	
		0.037	0.121	7.5			0.111	0.362	7.5	
		0.019	0.129	3.6			0.090	0.612	3.6	
		0.015	0.153	2.4			0.085	0.867	2.4	
		0.009	0.184	1.2			0.100	2.04	1.2	
							0.066	5.38	0.6	
.25		13.2	10.8	30.1	29.4					
		6.7	10.9	15.0						
		1.5	4.9	7.5						
		0.6	4.1	3.6						
		0.4	4.1	2.4						
		0.2	4.1	1.2						
.30							19	15.5	30.1	0.0
							7.3	11.9	15.0	
							3.0	9.8	7.5	
							1.9	12.9	3.6	
							0.9	9.2	2.4	
							0.7	14.3	1.2	
							0.2	16.3	0.6	

* No yield point values given

TABLE IV (*continued*)

Concentration	Yield point (dyne·cm.$^{-2}$)	Torque (gm.-cm.)	Apparent viscosity coeff. (poise)	Shear strain (rate)	Thixotropy coeff.	Yield point (dyne·cm.$^{-2}$)	Torque (gm.-cm.)	Apparent viscosity coeff. (poise)	Shear strain (rate)	Thixotropy coeff.
		No. 3 fraction (5 me. NaOH)*					No. 4 fraction (5 me. NaOH)*			
.002		0.0121	0.0099	30.1	0.0		0.0128	0.0104	30.1	0.0
		0.0048	0.0098	15.0			0.0054	0.0089	15.0	
		0.0030	0.0098	7.5			0.0030	0.0098	7.5	
		0.0018	0.0122	3.6			0.0017	0.0115	3.6	
							0.0009	0.0092	2.4	
.005		0.0124	0.0101	30.1	0.0		0.0120	0.0098	30.1	0.0
		0.0052	0.0089	15.0			0.0056	0.0091	15.0	
		0.0032	0.0104	7.5			0.0038	0.0124	7.5	
		0.0017	0.0102	3.6			0.0017	0.0115	3.6	
							0.0013	0.0133	2.4	
							0.0006	0.0122	1.2	
.01		0.0124	0.0101	30.1	0.0		0.0123	0.0100	30.1	0.024
		0.0056	0.0091	15.0			0.0066	0.0108	15.0	
		0.0033	0.0108	7.5			0.0030	0.0098	7.5	
		0.0020	0.0136	3.6			0.0023	0.0156	3.6	
.02		0.0128	0.0104	30.1	0.0		0.0133	0.0108	30.1	0.0
		0.0060	0.0098	15.0			0.0063	0.0103	15.0	
		0.0036	0.0118	7.5			0.0035	0.0114	7.5	
		0.0020	0.0136	3.6			0.0022	0.0115	3.6	
.03		0.017	0.014	30.1	0.0		0.015	0.012	30.1	0.0
		0.007	0.011	15.0			0.006	0.010	15.0	
		0.001	0.009	7.5			0.005	0.016	7.5	
							0.002	0.014	3.6	
.06		0.019	0.015	30.1	0.03		0.017	0.014	30.1	0.0
		0.010	0.016	15.0			0.006	0.010	15.0	
		0.002	0.009	7.5			0.002	0.009	7.5	
		0.001	0.009	3.6			0.001	0.009	3.6	
.10		0.025	0.020	30.1	0.0		0.020	0.016	30.1	0.088
		0.012	0.020	15.0			0.012	0.019	15.0	
		0.002	0.009	7.5			0.004	0.013	7.5	
		0.001	0.009	3.6			0.002	0.014	3.6	
.13		0.027	0.022	30.1	0.21				30.1	101
		0.018	0.029	15.0					15.0	
		0.010	0.033	7.5					7.5	
		0.001	0.009	3.6						
.15		0.051	0.042	30.1	0.21				30.1	97
		0.030	0.049	15.0					15.0	
		0.023	0.075	7.5					7.5	
		0.012	0.082	3.6						
		0.008	0.0816	2.4						
		0.003	0.061	1.2						
		0.001	0.081	0.6						
.20		0.386	0.314	30.1	7.44		2.5	2.04	30.1	50
		0.348	0.567	15.0			2.3	3.75	15.0	
		0.270	0.880	7.5			2.0	6.52	7.5	
		0.220	1.49	3.6			1.7	11.6	3.6	
		0.204	2.08	2.4			1.6	16.3	2.4	
		0.180	3.67	1.2			1.4	28.6	1.2	
		0.120	9.80	0.6			0.9	73.4	0.6	
.25		1.6	1.30	30.1	25.0		16.6	13.5	30.1	312
		1.32	2.15	15.0			14.8	24.1	15.0	
		1.10	3.59	7.5			12.2	39.8	7.5	
		0.92	6.26	3.6			10.4	70.7	3.6	
		0.84	8.57	2.4			9.6	97.9	2.4	
		0.68	13.9	1.2			8.5	173.4	1.2	
		0.42	34.3	0.6			4.8	391	0.6	
.30		30.8	25.1	30.1	0.0					
		9.0	14.7	15.0						
		4.6	15.0	7.5						
		3.7	25.2	3.6						
		3.2	32.6	2.4						
		2.4	49.0	1.2						
		1.1	89.7	0.6						

TABLE IV (*concluded*)

Concentration	Yield point (dyne·cm.$^{-2}$)	Torque (gm.-cm.)	Apparent viscosity coeff. (poise)	Shear strain (rate)	Thixotropy coeff.	Yield point (dyne·cm.$^{-2}$)	Torque (gm.-cm.)	Apparent viscosity coeff. (poise)	Shear strain (rate)	Thixotropy coeff.
		No. 5 fraction (5 me. NaOH)†					No. 6 fraction (9 me. NaOH)*			
.002		0.0122	0.0099	30.1	0.0		0.0117	0.0095	30.1	0.0
		0.0060	0.0098	15.0			0.0053	0.0089	15.0	
		0.0032	0.0104	7.5			0.0027	0.0089	7.5	
		0.0026	0.0177	3.6			0.0014	0.0095	3.6	
		0.0020	0.0204	2.4			0.0012	0.0122	2.4	
		0.0012	0.0245	1.2			0.0008	0.015	1.2	
.005	0.023	0.0356	0.0290	30.1	0.294		0.0117	0.0095	30.1	0.009
		0.0242	0.0394	15.0			0.006	0.0098	15.0	
		0.0182	0.0596	7.5			0.0034	0.0111	7.5	
		0.0140	0.095	3.6			0.0020	0.0136	3.6	
		0.0130	0.133	2.4			0.0014	0.0143	2.4	
		0.0104	0.212	1.2			0.0009	0.0184	1.2	
.01		0.013	0.011	30.1	0.059		0.0137	0.0112	30.1	0.0
		0.008	0.013	15.0			0.0068	0.0111	15.0	
		0.001	0.003	7.5			0.0037	0.0121	7.5	
							0.0023	0.0156	3.6	
							0.0016	0.0163	2.4	
							0.0012	0.025	1.2	
.02		0.016	0.013	30.1	0.059		0.0132	0.0108	30.1	0.0
		0.009	0.015	15.0			0.0060	0.0098	15.0	
		0.005	0.016	7.5			0.0036	0.0107	7.5	
		0.002	0.014	3.6			0.0018	0.0122	3.6	
							0.0014	0.0143	2.4	
							0.0011	0.0224	1.2	
.03		0.017	0.014	30.1	0.059		0.017	0.014	30.1	0.0
		0.010	0.016	15.0			0.008	0.013	15.0	
		0.005	0.016	7.5						
		0.002	0.014	3.6						
.06		0.023	0.019	30.1	0.088		0.025	0.020	30.1	0.088
		0.010	0.016	15.0			0.014	0.023	15.0	
		0.007	0.023	7.5			0.006	0.019	7.5	
		0.002	0.014	3.6						
.10		0.035	0.029	30.1	0.029		0.040	0.033	30.1	0.029
		0.017	0.028	15.0			0.021	0.034	15.0	
		0.007	0.023	7.5			0.013	0.042	7.5	
		0.002	0.014	3.6			0.005	0.034	3.6	
.13				30.1			0.059	0.048	30.1	0.177
				15.0			0.033	0.054	15.0	
				7.5			0.019	0.062	7.5	
							0.010	0.068	3.6	
.15		0.069	0.056	30.1	1.18		0.071	0.058	30.1	0.0
		0.037	0.060	15.0			0.033	0.054	15.0	
		0.028	0.091	7.5			0.015	0.049	7.5	
		0.009	0.061	3.6			0.014	0.095	3.6	
		0.006	0.061	2.4						
		0.002	0.041	1.2						
.20		0.154	0.126	30.1	4.11		0.226	0.184	30.1	1.50
		0.086	0.140	15.0			0.144	0.235	15.0	
		0.047	0.153	7.5			0.089	0.290	7.5	
		0.025	0.176	3.6			0.055	0.374	3.6	
		0.017	0.173	2.4			0.034	0.347	2.4	
		0.010	0.204	1.2			0.018	0.367	1.2	
		0.002	0.162	0.6			0.006	0.489	0.6	

† At 0.005 concentration, yield point is 0.023 dyne·cm.$^{-2}$

(Continued from p. 157)

$\frac{dv}{dr}$ = rate of shear.
S = angular velocity of outer cup (revolutions/sec.).
r_1 = radius of inner cylinder (0.99 cm.).
r_2 = radius of outer cylinder (1.52 cm.).

$$\frac{dv}{dr} = \frac{1.52 \times 6.28}{0.53} S = 18.0S$$

The rate of shear for the various speeds, therefore, is obtained from the product of the angular velocity in revolutions per second and the factor 18.0. Table V gives the rate of shear strain and the reciprocal rate for various speeds of the viscosimeter.

TABLE V

Viscosimeter speed (r.p.m.)	Shear strain (rate)	Shear strain (reciprocal rate)
100	30.1	0.033
50	15.0	0.067
25	7.5	0.133
12	3.6	0.322
8	2.4	0.417
4	1.2	0.834
2	0.6	1.67
1	0.3	3.33

The angle of twist of each wire used in the instrument was translated into gram-centimeters of torque by direct measurement. The relation between torque and viscosity was obtained by calibration with sucrose solutions and oils of known viscosity. The average factor obtained to relate torque to coefficient of viscosity thus was 0.815 for speeds of 100 r.p.m.

An example will clarify the calculations. Using the No. 6 H-kaolin fraction (Table IV, p. 160) at a concentration of 0.002 by volume, the rate of shear strain at a viscosimeter speed of 100 r.p.m. from Table V is 30.1 and the apparent viscosity (in poises) is obtained by the product of the torque (gm.-cm.) and the factor of 0.815, which has been determined from calibration charts, giving the relationship between torque and viscosity. Thus at the shear rate of 30.1, the torque obtained on this suspension was 0.0122 gm.-cm. The apparent viscosity is equal to 0.0122 × 0.815 or 0.0995 poise.

The calculation of the yield point was made by assuming that the end effects could be neglected as discussed by Barr.[15] The relation for the yield point may be expressed as follows:

$$YP \text{ (dynes·cm.}^{-2}) = \frac{\text{torque (gm.-cm.) } 980.4}{\text{area (cm.}^2)}$$

Area $= 2\pi r_1 h$
$r_1 = 0.99$
$h = 5.37$

$$YP = \frac{980.4 \text{ torque}}{2\pi \times 0.99 \times 5.37} = 29.35 \text{ torque}.$$

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[15] Guy Barr, Monograph of Viscometry. Oxford Univ. Press, London, 1931; *Ceram. Abs.*, **10** [9] 665 (1931).

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